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(71) Applicants: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL [US/US]; Office of Technology Development, Campus Box 4105, 308 Bynum Hall, Chapel Hill, NC 27599-4105 (US).

- (72) Inventors: JOHNSON, Lynda, Kaye; Apartment 5B2, 402 Foulk Road, Wilmington, DE 19803-3805 (US). KILLIAN, Christopher, Moore; 406 Summerwalk Circle, Chapel Hill, NC 27514 (US). ARTHUR, Samuel, David; 3214 North Monroe Street, Wilmington, DE 19802-2654 (US). FELD-MAN, Jerald; 16 Cinnamon Drive, Hockessin, DE 19707-1349 (US). McCORD, Elizabeth, Forrester, 514 Hemlock Drive, Hockessin, DE 19707-9361 (US). McLAIN, Stephan, James; 202 Old Mill Lane, Wilmington, DE 19803-4922 (US). KREUTZER, Kristina, Ann; Apartment 2C, 4 Doe Run Court, Wilmington, DE 19808-2059 (US). BEN-NETT, Margaret, Anne; 1 Brandywine Falls, Wilmington, DE 19806 (US). COUGHLIN, Edward, Bryan; Apartment E, 2227 Prior Road, Wilmington, DE 19809 (US). ITTEL, Steven, Dale; 2802 Landon Drive, Wilmington, DE 19810-2213 (US). PARTHASARATHY, Anju; 1562 Pottstown Pike, Glenmoore, PA 19343-9614 (US). TEMPEL, Daniel, Joseph; Apartment 10, 400 Davie Road, Carrboro, NC 27510 (US). BROOKHART, Maurice, S.; 944 Old Orchard Road, Chapel Hill, NC 27514 (US).
- (74) Agents: EVANS, Craig, H. et al.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).
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(54) Title: α-OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR

(57) Abstract

Disclosed herein are processes for polymerizing ethylene, acyclic olefins, and/or selected cyclic olefins, and optionally selected olefinic esters or carboxylic acids, and other monomers. The polymerizations are catalysed by selected transition metal compounds, and sometimes other co-catalysts. Since some of the polymerizations exhibit some characteristics of living polymerizations, block copolymers can be readily made. Many of the polymers produced are often novel, particularly in regard to their microstructure, which gives some of them unusual properties. Numerous novel catalysts are disclosed, as well as some novel processes for making them. The polymers made are useful as elastomers, molding resins, in adhesives, etc. Also described herein is the synthesis of linear α-olefins by the oligomerization of ethylene using as a catalyst system a combination of a nickel compound having a selected \alpha-dilmine ligand and a selected Lewis or Bronsted acid, or by contacting selected \$(a)-diimine nickel complexes with ethylene.

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TITLE

 α -OLEFINS AND OLEFIN POLYMERS AND PROCESSES THEREFOR This application is a continuation-in-part of pending prior application Serial No. 60/002,654, filed 5 August 22, 1995, is also a continuation-in-part of pending application Serial No. 60/007,375, filed August 8, 1995, is also a continuation-in-part of pending application Serial No. 08/473,590, filed June 7, 1995, which is a continuation-in-part of prior pending application Serial No. 08/415,283, filed April 3, 1995, which is a continuation-in-part of pending prior application Serial No. 08/378,044 filed January 24, 1995.

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FIELD OF THE INVENTION

The invention concerns novel homo- and copolymers 15 of ethylene and/or one or more acyclic olefins, and/or selected cyclic olefins, and optionally selected ester, carboxylic acid, or other functional group containing olefins as comonomers; selected transition metal containing polymerization catalysts; and processes for 20 making such polymers, intermediates for such catalysts, and new processes for making such catalysts. disclosed herein is a process for the production of linear alpha-olefins by contacting ethylene with a nickel compound of the formula [DAB] NiX2 wherein DAB is 25 a selected α -diimine and X is chlorine, bromine, iodine or alkyl, and a selected Lewis or Bronsted acid, or by contacting ethylene with other selected α -diimine nickel complexes

BACKGROUND OF THE INVENTION

Homo- and copolymers of ethylene (E) and/or one or more acyclic olefins, and/or cyclic olefins, and/or substituted olefins, and optionally selected olefinic esters or carboxylic acids; and other types of monomers, are useful materials, being used as plastics for packaging materials, molded items, films, etc., and as elastomers for molded goods, belts of various types, in tires, adhesives, and for other uses. It is well

known in the art that the structure of these various polymers, and hence their properties and uses, are highly dependent on the catalyst and specific conditions used during their synthesis. In addition to these factors, processes in which these types of polymers can be made at reduced cost are also important. Therefore, improved processes for making such (new) polymers are of interest. Also disclosed herein are uses for the novel polymers.

 α -Olefins are commercial materials being particularly useful as monomers and as chemical intermediates. For a review of α -olefins, including their uses and preparation, see B. Elvers, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. Al3, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 238-251. They are useful as chemical intermediates and they are often made by the oligomerization of ethylene using various types of catalysts. Therefore catalysts which are capable or forming α -olefins from ethylene are constantly sought.

SUMMARY OF THE INVENTION

This invention concerns a polyolefin, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

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This invention also concerns a polyolefin which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches.

Disclosed herein is a polymer, consisting essentially of repeat units derived from the monomers,

ethylene and a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen, hydrocarbyl or substituted hydrocarbyl, and m is 0 or an integer from 1 to 16, and which contains about 0.01 to about 40 mole percent of repeat units derived from said compound, and provided that said repeat units derived from said compound are in branches of the formula $-CH(CH_2)_nCO_2R^1$, in about 30 to about 70 mole percent of said branches n is 5 or more, in about 0 to about 20 mole percent n is 4, in about 3 to 60 mole percent n is 1, 2 and 3, and in about 1 to about 60 mole percent n is 0.

This invention concerns a polymer of one or more alpha-olefins of the formula $CH_2=CH(CH_2)_aH$ wherein a is an integer of 2 or more, which contains the structure (XXV)

$$\begin{array}{cccc} R^{35} & R^{36} \\ | & | \\ --CH-CH_2-CH--- & (XXV) \end{array}$$

wherein R^{35} is an alkyl group and R^{36} is an alkyl group containing two or more carbon atoms, and provided that R^{35} is methyl in about 2 mole percent or more of the total amount of (XXV) in said polymer.

This invention also includes a polymer of one or more alpha-olefins of the formula $\mathrm{CH_2=CH\,(CH_2)_{a}H}$ wherein a is an integer of 2 or more, wherein said polymer contains methyl branches and said methyl branches comprise about 25 to about 75 mole percent of the total branches.

This invention also concerns a polyethylene containing the structure (XXVII) in an amount greater than can be accounted for by end groups, and preferably at least 0.5 or more of such branches per 1000 methylene groups than can be accounted for by end groups.

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This invention also concerns a polypropylene containing one or both of the structures (XXVIII) and (XXIX) and in the case of (XXIX) in amounts greater than can be accounted for by end groups. Preferably at least 0.5 more of (XXIX) branches per 1000 methylene groups than can be accounted for by end groups, and/or at least 0.5 more of (XXVIII) per 1000 methylene groups are present in the polypropylene.

Also described herein is an ethylene homopolymer with a density of 0.86 g/ml or less.

Described herein is a process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of

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(XXIII)

$$\begin{array}{c|c}
R^{20} \\
 & H \\
R^{21} & N \\
 & R^{22} & N \\
 & O & H \\
 & R^{23}
\end{array}$$

(XXXII)

with an olefin wherein:

said olefin is selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹CH=CHR¹⁷, cyclobutene, cyclopentene, norbornene, or substituted norbornene;

said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or \mbox{R}^3 and \mbox{R}^4

taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

R⁴⁵ is hydrocarbyl or substituted hydrocarbyl, and R²⁹ is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring; each R³⁰ is independently hydrogen, substituted

10 hydrocarbyl or hydrocarbyl, or two of R³⁰ taken together form a ring;

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen,

15 hydrocarbyl or substituted hydrocarbyl;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

n is 2 or 3;

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R¹ is hydrogen, hydrocarbyl or substituted
hydrocarbyl;

and provided that:

25 said transition metal also has bonded to it a ligand that may be displace by said olefin or add to said olefin;

when M is Pd, said bidentate ligand is (VIII),
(XXXII) or (XXIII);

when M is Pd a diene is not present; and when norbornene or substituted norbornene is used no other olefin is present.

Described herein is a process for the copolymerization of an olefin and a fluorinated olefin, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of

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with an olefin, and a fluorinated olefin wherein:

said olefin is selected from the group consisting of ethylene and an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$;

said transition metal is selected from the group consisting of Ni and Pd;

said fluorinated olefin is of the formula $H_2C=CH\left(CH_2\right){}_aR_fR^{42};$

a is an integer of 2 to 20; R_f is perfluoroalkylene optionally containing one or more ether groups;

R42 is fluorine or a functional group;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring;

each R¹⁷ is independently saturated

25 hydrocarbyl;

and provided that said transition metal also has bonded to it a ligand that may be displaced by said olefin or add to said olefin.

This invention also concerns a copolymer of an olefin of the formula $R^{17}CH=CHR^{17}$ and a fluorinated olefin of the formula $H_2C=CH(CH_2)_aR_fR^{42}$, wherein:

each R^{17} is independently hydrogen or saturated hydrocarbyl;

a is an integer of 2 to 20; $R_{\rm f}$ is perfluoroalkylene optionally containing one or more ether groups; and

 R^{42} is fluorine or a functional group; provided that when both of R^{17} are hydrogen and R^{42} is fluorine, R_f is $-(CF_2)_b$ - wherein b is 2 to 20 or perfluoroalkylene containing at least one ether group.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

25 wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd the m oxidation state;

y + z = m

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that:

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when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

$$R^{3}$$
 R^{2}
 R^{4}
 R^{5}
 R^{2}
 R^{5}
 R^{7}
 R^{2}
 R^{4}
 R^{5}
 R^{2}
 R^{5}
 R^{5}
 R^{7}
 R^{7}
 R^{2}
 R^{7}
 R^{7

5 or

(III)

(IV)

wherein:

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(II)

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^2 is hydrogen, hydrocarbyl not containing clefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

20 n is 2 or 3;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion; R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

each R¹⁶ is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

R⁸ is hydrocarbyl; and

 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

and provided that:

when M is Pd a diene is not present; and when norbornene or substituted norbornene is used no other monomer is present.

This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH2 or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

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$$R^{20}$$
 R^{28}
 R^{28}
 R^{20}
 R^{29}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{21}
 R^{22}
 R^{23}
 R^{20}
 R^{20}
 R^{21}
 R^{22}
 R^{22}
 R^{23}
 R^{23}
 R^{21}
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 R^{23}
 R^{21}
 R^{23}
 R^{23}
 R^{23}
 R^{21}
 R^{23}
 R^{23}

wherein:

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 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

 \mbox{R}^{45} is hydrocarbyl or substituted hydrocarbyl, and \mbox{R}^{29} is hydrogen, substituted hydrocarbyl or

hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}CC(=0)$ -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6; and

X is a weakly coordinating anion; and provided that:

10 when M is Pd or (XVIII) is used a diene is not present; and

in (XVII) M is not Pd.

This invention includes a process for the production of polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

$$\begin{array}{c|c}
R^{20} \\
 & H \\
 & R^{21} \\
 & N \\
 & Pd \\
 & R^{22} \\
 & N \\
 & X \\
 & R^{23}
\end{array}$$

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(XVIII)

wherein:

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C$ (=0) - or $R^{15}OC$ (=0) -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

and provided that:

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when M is Pd a diene is not present; and when norbornene or substituted norbornene is used no other monomer is present.

Described herein is a process for the production for polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C,

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, V, Cr, a rare earth metal, Co, Fe, Sc, or Ni, of oxidation state m;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

 R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R³⁰ is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R³⁰ taken together form a ring;

n is 2 or 3;

y and z are positive integers;

y+z=m;

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each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present.

Disclosed herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about -100° C to about $+200^{\circ}$ C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted

norbornene, and norbornene; optionally a source of X; with a compound of the formula

$$\begin{array}{c|cccc}
R^3 & R^2 & R^2 & R^3 \\
\hline
 & N & T^1 & R^2 & R^3 \\
\hline
 & N & Pd & E & Pd & N & R^3 \\
\hline
 & N & R^5 & R^5 & R^4 & X
\end{array}$$
(V)

wherein:

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 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds;

T¹ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -;
R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

E is halogen or -OR18;

 R^{18} is hydrocarbyl not containing olefinic or 25 acetylenic bonds; and

X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ

or WS', provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

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and one or more monomers selected from the

10 group consisting of ethylene, an olefin of the formula

R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, 4-vinylcyclohexene,

cyclobutene, cyclopentene, substituted norbornene, or
norbornene;

wherein:

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M is Ni(II), Co(II), Fe(II), or Pd(II);

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or

30 bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Included herein is a polymerization process, comprising, contacting a compound of the formula $[Pd(R^{13}CN)_4]\,X_2 \ \text{or a combination of} \ Pd[OC(O)\,R^{40}]_2 \ \text{and} \ HX; \ a compound of the formula}$

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and Rⁱ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds;

R¹³ is hydrocarbyl;

 R^{40} is hydrocarbyl or substituted hydrocarbyl and

X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Also described herein is a polymerization process, comprising;

contacting Ni[0], Pd[0] or Ni[I] compound containing a ligand which may be displaced by a ligand of the formula (VIII), (XXX), (XXXII) or (XXIII);

a second compound of the formula

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or

(XXXII)

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an oxidizing agent;

a source of a relatively weakly coordinating
anion:

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene;

wherein:

10 R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R¹³ is hydrocarbyl;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

 R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

 R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

n is 2 or 3;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

15 X is a weakly coordinating anion;
 provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when said Pd[0] compound is used, a diene is not present; and

when said second compound is (XXX) only an Ni[0] or Ni[I] compound is used.

Described herein is a polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), oxygen, an alkyl aluminum compound, and a compound of the formula

30 (VIII)

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula

R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or \mbox{R}^3 and \mbox{R}^4 taken together are hydrocarbylene or substituted

hydrocarbylene to form a ring; and

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each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

A polymerization process, comprising, contacting oxygen and an alkyl aluminum compound, or a compound of the formula HX, and a compound of the formula

R³

$$R^2$$
 R^3
 R^3

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

X is a weakly coordinating anion; and provided that, when norbornene or substituted norbornene is present, no other monomer is present.

Described herein is a polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), HX or a Bronsted acidic solid, and a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; and

X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

XIX

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

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M is Ni(II) or Pd(II);

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or atleast two saturated carbon atoms;

10 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula

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(XIV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that R¹⁷ contains no olefinic bonds; and

each R²⁷ is independently hydrocarbyl; each X is a weakly coordinating anion; provided that, when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

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(XV)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

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R⁴⁶ and R⁴⁷ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^{48} and R^{49} are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each R³¹ is independently hydrocarbyl, substituted hydrocarbyl or hydrogen;

M is Ti, Zr, Co, V, Cr, a rare earth metal, Fe,

10 Sc, Ni, or Pd of oxidation state m;

y and z are positive integers;

y+z = m;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

20 S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

Disclosed herein is a compound of the formula

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wherein:

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 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion; and R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

provided that when R³ and R⁴ taken together are hydrocarbylene to form a carbocyclic ring, Z is not an organic nitrile.

Described herein is a compound of the formula

wherein:

R⁵⁰ is substituted phenyl;

R⁵¹ is phenyl or substituted phenyl;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

and provided that groups in the 2 and 6 positions of R^{50} have a difference in $E_{\rm s}$ of about 0.60 or more.

Described herein is a compound of the formula

(IVXXX)

wherein:

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R⁵² is substituted phenyl;

R⁵³ is phenyl or substituted phenyl;

 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted

10 hydrocarbylene to form a ring;

Q is alkyl, hydride, chloride, bromide or iodide:

S is alkyl, hydride, chloride, bromide or iodide;

15 and provided that;

groups in the 2 and 6 positions of R^{52} have a difference in E_s of 0.15 or more; and

when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to Ni.

This invention includes a compound of the formula

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wherein:

 $\mbox{\ensuremath{R}}^2$ and $\mbox{\ensuremath{R}}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom

bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

R¹⁵ is hydrocarbyl not containing an olefinic
or acetylenic bond;

Z is a neutral Lewis acid wherein the donating atom is nitrogen, sulfur or oxygen, provided that, if the donating atom is nitrogen, then the pKa of the conjugate acid of that compound is less than about 6; and

X is a weakly coordinating anion.

This invention also concerns a compound of the formula

wherein:

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 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

M is Ni(II) or Pd(II);

each R¹⁶ is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

X is a weakly coordinating anion; and

R⁸ is hydrocarbyl.

Also disclosed herein is a compound of the formula

$$\begin{array}{c|cccc}
R^3 & R^2 & R^2 & R^3 \\
\hline
 & N & T^1 & R^2 & R^3 \\
\hline
 & N & Pd & E & T1 & Pd & R^3 \\
\hline
 & N & R^5 & R^5 & R^4 & X^5
\end{array}$$
(V)

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wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

E is halogen or -OR18;

R¹⁸ is hydrocarbyl not containing olefinic or acetylenic bonds;

T¹ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion.

Included herein is a compound of the formula $[(\eta^4 - 1, 5 - COD) PdT^1Z]^*X^*$, wherein:

T¹ is hydrocarbyl not containing olefinic or acetylenic bonds;

X is a weakly coordinating anion; COD is 1,5-cyclooctadiene;

Z is R¹⁰CN; and

 ${\ensuremath{\mathsf{R}}}^{10}$ is hydrocarbyl not containing olefinic or acetylenic bonds.

Also included herein is a compound of the formula

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wherein:

M is Ni(II) or Pd(II);

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

T³ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH₂CH₂CO₂R⁸;

P is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when M is Pd(II), optionally one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^2$, CO, or a vinyl ketone;

R⁸ is hydrocarbyl;

m is 0 or an integer from 1 to 16;

R¹ is hydrogen, or hydrocarbyl or substituted
hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion; provided that, when M is Ni(II), R^{11} is not $-CO_2R^8$. Also described herein is a compound of the formula

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wherein:

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

 $\ensuremath{\text{R}^{\text{15}}}$ is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion.

Included herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

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M is Ni(II) or Pd(II);

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or \mbox{R}^3 and \mbox{R}^4 taken together are hydrocarbylene or substituted

15 hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

 T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R}^8\,;$

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula CH₂=CH(CH₂)_mCO₂R¹, CO or a vinyl ketone;

R⁸ is hydrocarbyl;

each R¹⁷ is independently hydrocarbyl or

30 substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 35 10 carbon atoms;

m is 0 or an integer of 1 to 16; and X is a weakly coordinating anion;

provided that:

when M is Pd a diene is not present;

when norbornene or substituted norbornene is present, no other monomer is present; and

further provided that, when M is Ni(II), \mathbf{R}^{11} is not

-CO₂R⁸.

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Included herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about -100°C to about +200°C, a compound of the formula

$$\begin{array}{c|ccccc}
R^{3} & & & & & & & \\
& & & & & & & & \\
N & & & & & & & \\
N & & & & & & & \\
N & & & & & & & \\
N & & & & & & & \\
N & & & & & & & \\
N & & & & & & & \\
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N & & & & & & & \\
N & & &$$

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

20 M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹¹ is independently hydrogen, or alkyl, or both of R¹¹ taken together are hydrocarbylene to form a carbocyclic ring;

T³ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH₂CH₂CO₂R⁸;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II), optionally one or more of: a compound of the formula CH₂=CH(CH₂)_mCO₂R¹, CO, or a vinyl ketone;

R⁸ is hydrocarbyl;

a is 1 or 2;

y + a + 1 = m;

each R¹⁷ is independently hydrocarbyl or

substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and X is a weakly coordinating anion; provided that:

when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and further provided that, when M is Ni(II), R^{11} is not

 $-CO_2R^8$.

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30 Also described herein is a compound of the formula

$$\begin{array}{c|ccccc}
R^{3} & R^{2} \\
N & (Q)_{y} & H \\
N & (Q)_{y} & (Q)_{y} & (Q)_{y} & H \\
N & (Q)_{y} & (Q)_{y} & (Q)_{y} & H \\
N & (Q)_{y} & (Q)_{y} & (Q)_{y} & (Q)_{y} & H \\
N & (Q)_{y} & (Q)_{y} & (Q)_{y} & (Q)_{y} & (Q)_{y} & (Q)_{y} \\
N & (Q)_{y} \\
N & (Q)_{y} & (Q)_{y}$$

wherein:

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M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, or alkyl, or both of R^{11} taken together are hydrocarbylene to form a carbocyclic ring;

 T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-CH_2CH_2CO_2R^8$;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and optionally, when M is Pd(II), one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, CO, or a vinyl ketone;

Q is a monovalent anion;
R⁸ is hydrocarbyl;

a is 1 or 2;

y + a + 1 = m;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and and X is a weakly coordinating anion;

and provided that when M is Pd a green is not present.

Described herein is a process, comprising, contacting, at a temperature of about -40° C to about $+60^{\circ}$ C, a compound of the formula $[(\eta^4-1,5-\text{COD})\,\text{PdT}^1\text{Z}]^{+}\text{X}^{-}$ and a diimine of the formula

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to produce a compound of the formula

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wherein:

 T^{1} is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

X is a weakly coordinating anion;

COD is 1,5-cyclooctadiene;

Z is R¹⁰CN;

 ${\ensuremath{\mathsf{R}}}^{10}$ is hydrocarbyl not containing olefinic or acetylenic bonds;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

Described herein is a process, comprising, contacting, at a temperature of about -80°C to about +20°C, a compound of the formula (η^4 -1,5-COD)PdMe₂ and a diimine of the formula

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to produce a compound of the formula

$$R^3$$
 N
 Pd
 Me
 R^4
 R^5

15 (XXXXI)

wherein:

COD is 1,5-cyclooctadiene;

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

Also disclosed herein is a compound of the formula

(XIV)

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wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it:

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R²⁷ is hydrocarbyl; and
each X is a weakly coordinating anion.
This invention includes a compound of the formula

R³ N T⁴ CHR¹⁴
R⁴ N R¹⁴HC X

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wherein:

M is Ni(II) or Pd(II);

R² and R⁵ are each independently hydrocarbyl or 25 substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or \mbox{R}^3 and \mbox{R}^4 taken

together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{14} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

R¹ is hydrogen, or hydrocarbyl or substituted
hydrocarbyl containing 1 to 10 carbon atoms;

 T^4 is alkyl, $-R^{60}C(O)OR^8$, $R^{15}(C=O)$ - or $R^{15}OC(=O)$ -

R¹⁵ is hydrocarbyl not containing olefinic or 10 acetylenic bonds;

R⁶⁰ is alkylene not containing olefinic or acetylenic bonds;

R⁸ is hydrocarbyl;;

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and X is a weakly coordinating anion;

and provided that when R^{14} is $-(CH_2)_mCO_2R^1$, or T^4 is not alkyl, M is Pd(II).

Described herein is a homopolypropylene with a glass transition temperature of -30°C or less, and containing at least about 50 branches per 1000 methylene groups.

This invention also concerns a homopolymer of cyclopentene having a degree of polymerization of about 30 or more and an end of melting point of about 100°C to about 320°C, provided that said homopolymer has less than 5 mole percent of enchained linear olefin containing pentylene units.

In addition, disclosed herein is a homopolymer or copolymer of cyclopentene that has an X-ray powder diffraction pattern that has reflections at approximately 17.3° , 19.3° , 24.2° , and 40.7° 2θ .

Another novel polymer is a homopolymer of cyclopentene wherein at least 90 mole percent of enchained cyclopentylene units are 1,3-cyclopentylene units, and said homopolymer has an average degree of polymerization of 30 more.

Described herein is a homopolymer of cyclopentene wherein at least 90 mole percent of enchained cyclopentylene units are cis-1,3-cyclopentylene, and

said homopolymer has an average degree of polymerization of about 10 or more.

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Also described is a copolymer of cyclopentene and ethylene wherein at least 75 mole percent of enchained cyclopentylene units are 1,3-cyclopentylene units.

This invention concerns a copolymer of cyclopentene and ethylene wherein there are at least 20 branches per 1000 methylene carbon atoms.

Described herein is a copolymer of cyclopentene and ethylene wherein at least 50 mole percent of the repeat units are derived from cyclopentene.

Disclosed herein is a copolymer of cyclopentene and an α -olefin.

This invention also concerns a polymerization

15 process, comprising, contacting an olefin of the
formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, wherein each R¹⁷ is
independently hydrogen, hydrocarbyl, or substituted
hydrocarbyl provided that any olefinic bond in said
olefin is separated from any other olefinic bond or
20 aromatic ring by a quaternary carbon atom or at least
two saturated carbon atoms with a catalyst, wherein
said catalyst:

contains a nickel or palladium atom in a positive oxidation state;

contains a neutral bidentate ligand coordinated to said nickel or palladium atom, and wherein coordination to said nickel or palladium atom is through two nitrogen atoms or a nitrogen atom and a phosphorous atom; and

said neutral bidentate ligand, has an Ethylene Exchange Rate of less than 20,000 L-mol⁻¹s⁻¹ when said catalyst contains a palladium atom, and less than 50,000 L-mol⁻¹s⁻¹ when said catalyst contains a nickel atom;

35 and provided that when Pd is present a diene is not present.

Described herein is a process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound which is a salt of an alkali metal cation and a relatively noncoordinating monoanion;

a second compound of the formula

10 (XX)

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bond;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

S is chloride, iodide, or bromide; and provided that, when norbornene or substituted norbornene is present, no_other monomer is present.

Described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH(CH_2)_eG$ by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or $-CO_2R^1$; each e is independently 0 or an integer of 1 to

each R¹ is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G . is hydrogen; and

except when no branches should be theoretically present, the number of branches per 1000 methylene groups is 90% or less than the number of theoretical branches per 1000 methylene groups, or the number of

20 branches per 1000 methylene groups is 110% or more of theoretical branches per 1000 methylene groups, and

when there should be no branches theoretically present, said polyolefin has 50 or more branches per 1000 methylene groups;

and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

Also described herein is a polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH(CH_2)_eG$ by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or $-CO_2R^1$; each e is independently 0 or an integer of 1 to

35 20;

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20;

R¹ is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that:

said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G
is hydrogen;

said polymer has at least 50 branches of the formula $-(CH_2)_f G$ per 1000 methylene groups, wherein when G is the same as in a monomer and e $\neq f$, and/or for any single monomer of the formula $H_2C=CH(CH_2)_e G$ there are less than 90% of the number of theoretical branches per 1000 methylene groups, or more than 110% of the theoretical branches per 1000 methylene groups of the formula $-(CH_2)_f G$ and f=e, and wherein f is 0 or an integer of 1 or more;

and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms.

This invention concerns a process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

20 ethylene;

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a first compound W, which is a neutral Lewis acid capable of abstracting X to form WX, provided that the anion formed is a weakly coordinating anion, or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; and

a second compound of the formula

(XXXI)

wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or \mbox{R}^3 and \mbox{R}^4 taken

together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

Q and S are each independently chlorine, bromine, iodine or alkyl; and

wherein an α -olefin containing 4 to 40 carbon atoms is produced.

This invention also concerns a process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

ethylene and a compound of the formula

(III)

or

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(VXXXIV)

wherein:

20 R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl;

 \mbox{R}^3 and \mbox{R}^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or \mbox{R}^3 and \mbox{R}^4 taken together are hydrocarbylene or substituted

25 hydrocarbylene to form a ring;

T¹ is hydrogen or n-alkyl containing up to 38 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if

the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6:

U is n-alkyl containing up to 38 carbon atoms;

5 and

X is a noncoordinating anion;

and wherein an α -olefin containing 4 to 40 carbon atoms is produced.

Another novel process is a process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

ethylene;

and a Ni[II] of

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R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

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 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring and

wherein an α -olefin containing 4 to 40 carbon 25 atoms is produced.

Also described herein is a process for the production of polyolefins, comprising, contacting, at a temperature of about 0°C to about +200°C, a compound of the formula

$$R^3$$
 N
 A
 R^5
 X

XXXVII

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

10 R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

and X is a weakly coordinating anion;
and provided that:

when M is Pd a diene is not present; and when norbornene or substituted norbornene is present, no other monomer is present.

The invention also includes a compound of the formula

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$$\mathbb{R}^3$$
 \mathbb{N}
 \mathbb{R}^4
 \mathbb{N}
 \mathbb{R}^3
 \mathbb{N}
 \mathbb{R}^3

XXXVII

wherein:

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M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen,
10 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken
together are hydrocarbylene or substituted
hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

and X is a weakly coordinating anion; and provided that when M is Pd a diene is not present.

This invention also includes a compound of the formula

wherein:

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 ${
m R}^{54}$ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it:

each R⁵⁵ is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$:

each R¹⁷ is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and X is a weakly coordinating anion;

and provided that when M is Ni, W is alkylene and each \mathbb{R}^{17} is independently hydrogen or saturated hydrocarbyl.

This invention also includes a process for the production of a compound of the formula

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comprising, heating a compound of the formula

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at a temperature of about -30°C to about +100° for a sufficient time to produce (XXXVIII), and wherein:

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 ${
m R}^{54}$ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it:

each R⁵⁵ is independently hydrogen,

hydrocarbyl, substituted hydrocarbyl, or a functional
group;

 R^{56} is alkyl containing 2 to 30 carbon atoms; T^{5} is alkyl;

W is alkylene containing 2 to 30 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6; and

X is a weakly coordinating anion.

This invention also concerns a process for the polymerization of olefins, comprising, contacting a compound of the formula

(XXXVIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted

10 hydrocarbylene to form a ring;

R⁵⁴ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each R⁵⁵ is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula

25 R¹⁷CH=CHR¹⁷:

each R¹⁷ is independently hydrogen, saturated

X is a weakly coordinating anion;

hydrocarbyl or substituted saturated hydrocarbyl; and

and provided that:

when M is Ni, W is alkylene and each R¹⁷ is independently hydrogen or saturated hydrocarbyl;

and when norbornene or substituted norbornene is present, no other monomer is present.

This invention also concerns a homopolypropylene containing about 10 to about 700 δ + methylene groups per 1000 total methylene groups in said homopolypropylene.

Described herein is a homopolypropylene wherein the ratio of $\delta+:\gamma$ methylene groups is about 0.5 to about 7.

10 Also included herein is a homopolypropylene in which about 30 to about 85 mole percent of the monomer units are enchained in an ω ,1 fashion.

DETAILS OF THE INVENTION

Herein certain terms are used to define certain chemical groups or compounds. These terms are defined below.

- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.
- By "not containing olefinic or acetylenic bonds" is meant the grouping does not contain olefinic carbon-carbon double bonds (but aromatic rings are not excluded) and carbon-carbon triple bonds.
- e By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.
- By an alkyl aluminum compound is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide,

oxygen, and halogen may also be bound to aluminum atoms in the compound.

By "hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen.
 Typical hydrocarbylene groups are -(CH₂)₄-, CH₂CH(CH₂CH₃) CH₂CH₂- and

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If not otherwise stated, it is preferred that hydrocarbylene groups herein contain 1 to about 30 carbon atoms.

- By "substituted hydrocarbylene" herein is

 meant a hydrocarbylene group which contains one or more
 substituent groups which are inert under the process
 conditions to which the compound containing these
 groups is subjected. The substituent groups also do
 not substantially interfere with the process. If not
 otherwise stated, it is preferred that substituted
 hydrocarbylene groups herein contain 1 to about 30
 carbon atoms. Included within the meaning of
 "substituted" are heteroaromatic rings.
- By substituted norbornene is meant a

 25 norbornene which is substituted with one or more groups which does not interfere substantially with the polymerization. It is preferred that substituent groups (if they contain carbon atoms) contain 1 to 30 carbon atoms. Examples of substituted norbornenes are ethylidene norbornene and methylene norbornene.
 - By "saturated hydrocarbyl" is meant a univalent group containing only carbon and hydrogen which contains no unsaturation, such as olefinic, acetylenic, or aromatic groups. Examples of such groups include alkyl and cycloalkyl. If not otherwise

stated, it is preferred that saturated hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

- By "neutral Lewis base" is meant a compound, which is not an ion, which can act as a Lewis base. Examples of such compounds include ethers, amines, sulfides, and organic nitriles.
- By "cationic Lewis acid" is meant a cation which can act as a Lewis acid. Examples of such cations are sodium and silver cations.
- 10 By " α -olefin" is meant a compound of the formula CH_2 = CHR^{19} , wherein R^{19} is n-alkyl or branched alkyl, preferably n-alkyl.
- By "linear α -olefin" is meant a compound of the formula $CH_2=CHR^{19}$, wherein R^{19} is n-alkyl. It is preferred that the linear α -olefin have 4 to 40 carbon atoms.
 - By a "saturated carbon atom" is meant a carbon atom which is bonded to other atoms by single bonds only. Not included in saturated carbon atoms are carbon atoms which are part of aromatic rings.
 - By a quaternary carbon atom is meant a saturated carbon atom which is not bound to any hydrogen atoms. A preferred quaternary carbon atom is bound to four other carbon atoms.

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- By an olefinic bond is meant a carbon-carbon double bond, but does not include bonds in aromatic rings.
- By a rare earth metal is meant one of lanthanum, cerium, praeseodymium, neodymium,
 promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium.

This invention concerns processes for making polymers, comprising, contacting one or more selected olefins or cycloolefins, and optionally an ester or carboxylic acid of the formula $CH_2=CH(CH_2)_mCO_2R^2$, and other selected monomers, with a transition metal containing catalyst (and possibly other catalyst

components). Such catalysts are, for instance, various complexes of a diimine with these metals. By a "polymerization process herein (and the polymers made therein)" is meant a process which produces a polymer with a degree of polymerization (DP) of about 20 or more, preferably about 40 or more [except where otherwise noted, as in P in compound (VI)] By "DP" is meant the average number of repeat (monomer) units in the polymer.

One of these catalysts may generally be written as

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wherein: M is Ni(II), Co(II), Fe(II) or Pd(II); R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen,

20 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; Q is alkyl, hydride, chloride, iodide, or bromide; and S is alkyl, hydride, chloride, iodide, or bromide. Preferably M is Ni(II) or Pd(II).

In a preferred form of (I), R³ and R⁴ are each independently hydrogen or hydrocarbyl. If Q and/or S is alkyl, it is preferred that the alkyl contains 1 to 4 carbon atoms, and more preferably is methyl.

30 Another useful catalyst is

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wherein: R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R3 and R4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; T1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that, if the donating atom is nitrogen, then the pKa of the 15 conjugate acid of that compound is less than about 6; X is a weakly coordinating anion; and R15 is hydrocarbyl not containing olefinic or acetylenic bonds.

In one preferred form of (II), R^3 and R^4 are each independently hydrogen or hydrocarbyl. In a more preferred form of (II), T^1 is alkyl, and T^2 is especially preferably methyl. It is preferred that Z is $R^6_{\ 2}O$ or R^7CN , wherein each R^6 is independently hydrocarbyl and R^7 is hydrocarbyl. It is preferred that R^6 and R^7 are alkyl, and it is more preferred that they are methyl or ethyl. It is preferred that X^2 is BAF, X^2 SbF₆, PF₆ or BF₄.

Another useful catalyst is

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wherein: R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R3 and R4 are each independently hydrogen, hydrocarbyl, or substituted hydrocarbylene, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a 10 ring; T1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6; X is a weakly coordinating anion; and R15 is hydrocarbyl not containing olefinic or acetylenic bonds.

In one preferred form of (III), R^3 and R^4 are each independently hydrogen, hydrocarbyl. In a more preferred form of (III) T^1 is alkyl, and T^2 is especially preferably methyl. It is preferred that Z is R^6 ₂O or R^7 CN, wherein each R^6 is independently hydrocarbyl and R^7 is hydrocarbyl. It is preferred that R^6 and R^7 are alkyl, and it is especially preferred that they are methyl or ethyl. It is preferred that X^7 is BAF^7 , SbF_6 , PF_6 or BF_4 .

Relatively weakly coordinating anions are known to the artisan. Such anions are often bulky anions, particularly those that may delocalize their negative charge. Suitable weakly coordinating anions in this Application include $(Ph)_4B$ (Ph = phenyl), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (herein

abbreviated BAF), PF₆, BF₄, SbF₆, trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N^7$, and $(C_6F_5)_4B^7$. Preferred weakly coordinating anions include BAF⁷, PF₆, BF₄, and SbF₆.

Also useful as a polymerization catalyst is a compound of the formula

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wherein: R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; M is Ni(II) or Pd(II); each R¹⁶ is independently hydrogen or alkyl containing 1 to 10 carbon atoms; n is 1, 2, or 3; X is a weakly coordinating anion; and R⁸ is hydrocarbyl.

It is preferred that n is 3, and all of R^{16} are hydrogen. It is also preferred that R^8 is alkyl or substituted alkyl, especially preferred that it is alkyl, and more preferred that R^8 is methyl.

Another useful catalyst is

wherein: R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R3 and R4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R3 and R4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; T1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -; R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds; E is halogen or -OR18; R18 is hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. preferred that T is alkyl containing 1 to 4 carbon atoms, and more preferred that it is methyl. In other preferred compounds (V), R3 and R4 are methyl or hydrogen and R² and R⁵ are 2,6-diisopropylphenyl and X is BAF. It is also preferred that E is chlorine.

Another useful catalyst is a compound of the formula

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wherein: R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a

ring; T² is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -; R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds; and X is a weakly coordinating anion. In a more preferred form of (VII), T² is alkyl containing 1 to 4 carbon atoms and T² is especially preferably methyl. It is preferred that X is perfluoroalkylsulfonate, especially trifluoromethanesulfonate (triflate). If X is an extremely weakly coordinating anion such as BAF, (VII) may not form. Thus it may be said that (VII) forms usually with weakly, but perhaps not extremely weakly, coordinating anions.

In all compounds, intermediates, catalysts, processes, etc. in which they appear it is preferred that R² and R⁵ are each independently hydrocarbyl, and in one form it is especially preferred that R² and R⁵ are both 2,6-diisopropylphenyl, particularly when R³ and R⁴ are each independently hydrogen or methyl. It is also preferred that R³ and R⁴ are each independently hydrogen, hydrocarbyl or taken together hydrocarbylene to form a carbocyclic ring.

Compounds of the formula (I) wherein M is Pd, Q is alkyl and S is halogen may be made by the reaction of the corresponding 1,5-cyclooctadiene (COD) Pd complex with the appropriate diimine. When M is Ni, (I) can be made by the displacement of a another ligand, such as a dialkylether or a polyether such as 1,2-

30 dimethoxyethane, by an appropriate diimine.

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Catalysts of formula (II), wherein X is BAF, may be made by reacting a compound of formula (I) wherein Q is alkyl and S is halogen, with about one equivalent of an alkali metal salt, particularly the sodium salt, of HBAF, in the presence of a coordinating ligand, particularly a nitrile such as acetonitrile. When X is an anion such as BAF, SbF₆ or BF₄ the same

starting palladium compound can be reacted with the silver salt AgX.

However, sometimes the reaction of a diimine with a 1,5-COD Pd complex as described above to make compounds of formula (II) may be slow and/or give poor conversions, thereby rendering it difficult to make the starting material for (II) using the method described in the preceding paragraph. For instance when:

R²=R⁵=Ph₂CH- and R³=R⁴=H; R²=R⁵=Ph- and R³=R⁴=Ph; R²=R⁵=2-t-butylphenyl and R³=R⁴=CH₃; R²=R⁵=α-naphthyl and R³=R⁴=CH₃; and R²=R⁵=2-phenylphenyl and R³=R⁴=CH₃ difficulty may be encountered in making a compound of formula (II).

In these instances it has been found more convenient to prepare (II) by reacting $[(\eta^4-1,5-COD)PdT^1Z]^*X^-$, wherein T^1 and X are as defined above and Z is an organic nitrile ligand, preferably in an organic nitrile solvent, with a dimine of the formula

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By a "nitrile solvent" is meant a solvent that is at least 20 volume percent nitrile compound. The product of this reaction is (II), in which the Z ligand is the nitrile used in the synthesis. In a preferred synthesis, T^1 is methyl and the nitrile used is the same as in the starting palladium compound, and is more preferably acetonitrile. The process is carried out in solution, preferably when the nitrile is substantially all of the solvent, at a temperature of about -40° C to about $+60^{\circ}$ C, preferably about 0° C to about 30° C. It is

preferred that the reactants be used in substantially equimolar quantities.

The compound $[(\eta^4-1,5-COD)PdT^1Z]^{\dagger}X^{\dagger}$, wherein T^1 is alkyl, Z is an organic nitrile and X is a weakly coordinating anion may be made by the reaction of $[(\eta^4 -$ 1,5-COD) PdT¹A, wherein A is Cl, Br or I and T¹ is alkyl with the silver salt of X, AgX, or if X is BAF with an alkali metal salt of HBAF, in the presence of an organic nitrile, which of course will become the ligand -10 T¹. In a preferred process A is Cl, T¹ is alkyl, more preferably methyl, and the organic nitrile is an alkyl nitrile, more preferably acetonitrile. The starting materials are preferably present in approximately equimolar amounts, except for the nitrile which is 15 present preferably in excess. The solvent is preferably a non-coordinating solvent such as a halocarbon. Methylene chloride is useful as such a solvent. The process preferably is carried out at a temperature of about -40°C to about +50°C. preferred to exclude water and other hydroxyl 20 containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen.

Compounds of formula (II) [or (III) when the metal 25 is nickel] can also be made by the reaction of

30 with a source of the conjugate acid of the anion X, the acid HX or its equivalent (such as a trityl salt) in the presence of a solvent which is a weakly coordinating ligand such as a dialkyl ether or an alkyl

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> nitrile. It is preferred to carry out this reaction at about -80°C to about 30°C.

> Compounds of formula (XXXXI) can be made by a process, comprising, contacting, at a temperature of about -80°C to about +20°C, a compound of the formula (η^4 -1,5-COD) PdMe₂ and a diimine of the formula

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wherein: COD is 1,5-cyclooctadiene; R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R3 and R4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R3 and R4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring. It is preferred that the temperature is about -50°C to about +10°C. It is 20 also preferred that the two starting materials be used in approximately equimolar quantities, and/or that the reaction be carried out in solution. It is preferred that R² and R⁵ are both 2-t-butylphenyl or 2,5-di-tbutylphenyl and that R³ and R⁴ taken together are An, or R³ and R⁴ are both hydrogen or methyl.

Compounds of formula (IV) can be made by several routes. In one method a compound of formula (II) is reacted with an acrylate ester of the formula CH₂=CHCO₂R¹ wherein R¹ is as defined above. reaction is carried out in a non-coordinating solvent such as methylene chloride, preferably using a greater than 1 to 50 fold excess of the acrylate ester.

preferred reaction, Q is methyl, and R¹ is alkyl containing 1 to 4 carbon atoms, more preferably methyl. The process is carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification of the ingredients and keeping the process mass under an inert gas such as nitrogen

10 Alternatively, (IV) may be prepared by reacting (I), wherein Q is alkyl and S is Cl, Br or I with a source of an appropriate weakly coordinating anion such as AgX or an alkali metal salt of BAF and an acrylate ester (formula as immediately above) in a single step... Approximately equimolar quantities of (I) and the 15 weakly coordinating anion source are preferred, but the acrylate ester may be present in greater than 1 to 50 fold excess. In a preferred reaction, Q is methyl, and R¹ is alkyl containing 1 to 4 carbon atoms, 20 preferably methyl. The process is preferably carried out at a temperature of about -100°C to about +100°C, preferably about 0°C to about 50°C. It is preferred to exclude water and other hydroxyl containing compounds from the process, and this may be done by purification 25 of the ingredients and keeping the process mass under an inert gas such as nitrogen.

In another variation of the preparation of (IV) from (I) the source of the weakly coordinating anion is a compound which itself does not contain an anion, but which can combine with S [of (I)] to form such a weakly coordinating anion. Thus in this type of process by "source of weakly coordinating anion" is meant a compound which itself contains the anion which will become X, or a compound which during the process can combine with other process ingredients to form such an anion.

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Catalysts of formula (V), wherein X^{-} is BAF, may be made by reacting a compound of formula (I) wherein Q

is alkyl and S is halogen, with about one-half or an equivalent of an alkali metal salt, particularly the sodium salt, of HBAF. Alternatively, (V) containing other anions may be prepared by reacting (I), wherein Q is alkyl and S is Cl, Br or I with one-half equivalent of a source of an appropriate weakly coordinating anion such as AgX.

Some of the nickel and palladium compounds described above are useful in processes for polymerizing various olefins, and optionally also copolymerizing olefinic esters, carboxylic acids, or other functional olefins, with these olefins. is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a 15 weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting Q or S from (I) to form a weakly 20 coordination anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF5, Ar3B (wherein Ar is aryl), and BF1. By a cationic Lewis acid is meant a cation with a positive charge such as Aq', H', and Na'.

In those instances in which (I) (and similar catalysts which require the presence of a neutral Lewis acid or a cationic Lewis or Bronsted acid), does not contain an alkyl or hydride group already bonded to the metal (i.e., neither Q or S is alkyl or hydride), the neutral Lewis acid or a cationic Lewis or Bronsted acid also alkylates or adds a hydride to the metal, i.e., causes an alkyl group or hydride to become bonded to the metal atom.

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A preferred neutral Lewis acid, which can alkylate the metal, is a selected alkyl aluminum compound, such as R⁹₃Al, R⁹₂AlCl, R⁹AlCl₂, and "R⁹AlO" (alkylaluminoxanes), wherein R⁹ is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms.

Suitable alkyl aluminum compounds include methylaluminoxane (which is an oligomer with the general formula $[MeAlO]_n$), $(C_2H_5)_2AlCl$, $C_2H_5AlCl_2$, and $[(CH_3)_2CHCH_2]_3Al$.

Metal hydrides such as $NaBH_4$ may be used to bond hydride groups to the metal M.

The first compound and (I) are contacted, usually in the liquid phase, and in the presence of the olefin, and/or 4-vinylcyclohexene, cyclopentene, cyclobutene, substituted norbornene, or norbornene. The liquid phase may include a compound added just as a solvent and/or may include the monomer(s) itself. The molar ratio of first compound:nickel or palladium complex is about 5 to about 1000, preferably about 10 to about 100. The temperature at which the polymerization is carried out is about -100°C to about +200°C, preferably about -20°C to about +80°C. The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa, or more, being a suitable range. The pressure may affect the microstructure of the polyolefin produced (see below).

When using (I) as a catalyst, it is preferred that \mathbb{R}^3 and \mathbb{R}^4 are hydrogen, methyl, or taken together are

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It is also preferred that both R² and R⁵ are 2,6-disopropylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 4-methylphenyl, phenyl, 2,4,6-trimethylphenyl, and 2-t-butylphenyl. When M is Ni(II), it is preferred that Q and S are each independently chloride or bromide, while when M is Pd(II) it is preferred that Q is methyl, chloride, or bromide, and S is chloride, bromide or methyl. In

addition, the specific combinations of groups in the catalysts listed in Table I are especially preferred.

Table I

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R ²	R ³	R ⁵	R ^S			
K	R	R	R	Q	S	M
2,6-i-PrPh	H	H	2,6-i-PrPh	Me	Cl	Pd .
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Cl	Pd
2,6-i-PrPh	An	An	2,6-i-PrPh	Me	Cl	Pd
2,6-MePh	Н	Н	2,6-MePh	Me	Cl	Pd
4-MePh	H	Н	4-MePh	Me	Cl	Pd
4-MePh	Me	Me	4-MePh	Me	Cl	Pd
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	Me	Pđ
2,6-i-PrPh	Н	н	2,6-i-PrPh	Me	Me	₽d
2,6-MePh	Н	Н	2,6-MePh	Me	Me	Pd
2,6-i-PrPh	Н	Н	2,6-i-PrPh	Br	Br	Ni
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	H	H	2,6-MePh	Br	Br	Ni
Ph	Me	Me	Ph	Me	Cl	Pd
2,6-EtPh	Me	Me	2,6-EtPh	Me	Cl	Pđ
2,4,6-MePh	Me	Me	2,4,6-MePh	Me	Cl	Pd
2,6-MePh	Me	Me	2,6-MePh	Br	Br	Ni
2,6-i-PrPh	An	An	2,6-i-PrPh	Br	Br	Ni
2,6-MePh	An	An	2,6-MePh	Br	Br	Ni
2-t-BuPh	An	An	2-t-BuPh	Br	Br	Ni
2,5-t-BuPh	An	An	2,5-t-BuPh	Br	Br	Ni
2-i-Pr-6-MePh	An	An	2-i-Pr-6-MePh	Br	Br	Ni
2-i-Pr-6-MePh	Me	Me	2-i-Pr-6-MePh	Br	Br	Ni
2,6-t-BuPh	H ·	н	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	Me	Me	2,6-t-BuPh	Br	Br	Ni
2,6-t-BuPh	An	An	2,6-t-BuPh	Br	Br	Ni
		Me	2-t-BuPh	Br	Br	Ni

Note - In Tables I and II, and elsewhere herein, the following convention and abbreviations are used. For R² and R⁵, when a substituted phenyl ring is present, the amount of substitution is indicated by the number of numbers indicating positions on the phenyl

ring, so that, for example, 2,6-i-PrPh is 2,6-diisopropylphenyl. The following abbreviations are used: i-Pr = isopropyl; Me = methyl; Et = ethyl; t-Bu = t-butyl; Ph = phenyl; Np = naphthyl; An = 1,8-naphthylylene (a divalent radical used for both R³ and R⁴, wherein R³ and R⁴ taken together form a ring, which is part of an acenaphthylene group); OTf = triflate; and BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

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Preferred olefins in the polymerization are one or more of ethylene, propylene, 1-butene, 2-butene, 1-hexene 1-octene, 1-pentene, 1-tetradecene, norbornene, and cyclopentene, with ethylene, propylene and cyclopentene being more preferred. Ethylene (alone as a homopolymer) is especially preferred.

The polymerizations with (I) may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, monomer(s), and polymer may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, toluene and benzene.

Whether such a liquid is used, and which and how much liquid is used, may affect the product obtained. It may affect the yield, microstructure, molecular weight, etc., of the polymer obtained.

Compounds of formulas (XI), (XIII), (XV) and (XIX) may also be used as catalysts for the polymerization of the same monomers as compounds of formula (I). The polymerization conditions are the same for (XI), (XIII), (XV) and (XIX) as for (I), and the same Lewis and Bronsted acids are used as co-catalysts. Preferred groupings R^2 , R^3 , R^4 , and R^5 (when present) in (XI) and (XIII) are the same as in (I), both in a polymerization process and as compounds in their own right.

Preferred (XI) compounds have the metals Sc(III), Zr(IV), Ni(II), Ni(I), Pd(II), Fe(II), and Co(II). When M is Zr, Ti, Fe, and Sc it is preferred that all of Q and S are chlorine or bromine more preferably chlorine. When M is Ni or Co it is preferred that all of Q and S are chlorine, bromine or iodine, more preferably bromine.

In (XVII) preferred metals are Ni(II) and Ti(IV). It is preferred that all of Q and S are halogen. It is also preferred that all of R^{28} , R^{29} , and R^{30} are hydrogen, and/or that both R^{44} and R^{45} are 2,4,6-trimethylphenyl or 9-anthracenyl.

In (XV) it is preferred that both of R^{31} are hydrogen.

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In (XIII), (XXIII) and (XXXII) (as polymerization catalysts and as novel compounds) it is preferred that all of R²⁰, R²¹, R²² and R²³ are methyl. It is also preferred that T¹ and T² are methyl. For (XIII), when M is Ni(I) or (II), it is preferred that both Q and S are bromine, while when M is Pd it is preferred that Q is methyl and S is chlorine.

Compounds (II), (IV) or (VII) will each also cause the polymerization of one or more of an olefin, and/or a selected cyclic olefin such as cyclobutene, cyclopentene or norbornene, and, when it is a Pd(II) complex, optionally copolymerize an ester or carboxylic acid of the formula $CH_2=CH(CH_2)_mCO_2R^2$, wherein m is 0 or an integer of 1 to 16 and R^2 is hydrogen or hydrocarbyl or substituted hydrocarbyl, by themselves (without cocatalysts). However, (III) often cannot be used when the ester is present. When norbornene or substituted norbornene is present no other monomer should be present.

Other monomers which may be used with compounds

(II), (IV) or (VII) (when it is a Pd(II) complex) to
form copolymers with olefins and selected cycloolefins
are carbon monoxide (CO), and vinyl ketones of the
general formula H₂C=CHC(O)R²⁵, wherein R²⁵ is alkyl

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containing 1 to 20 carbon atoms, and it is preferred that R²⁵ is methyl. In the case of the vinyl ketones, the same compositional limits on the polymers produced apply as for the carboxylic acids and esters described as comonomers in the immediately preceding paragraph.

CO forms alternating copolymers with the various olefins and cycloolefins which may be polymerized with compounds (II), (IV) or (VII). The polymerization to form the alternating copolymers is done with both CO and the olefin simultaneously in the process mixture, and available to the catalyst. It is also possible to form block copolymers containing the alternating CO/(cyclo)olefin copolymers and other blocks containing just that olefin or other olefins or mixtures thereof. This may be done simply by sequentially exposing compounds (II), (IV) or (VII), and their subsequent living polymers, to the appropriate monomer or mixture of monomers to form the desired blocks. Copolymers of CO, a (cyclo)olefin and a saturated carboxylic acid or 20° ester of the formula $CH_2=CH\left(CH_2\right)_mCO_2R^1$, wherein m is 0 or an integer of 1 to 16 and R1 is hydrogen or hydrocarbyl or substituted hydrocarbyl, may also be made by simultaneously exposing the polymerization catalyst or living polymer to these 3 types of

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monomers.

The polymerizations may be carried out with (II), (III), (IV) or (VII), and other catalyst molecules or combinations, initially in the solid state [assuming (II), (III) (IV) or (VII) is a solid) or in solution. The olefin and/or cycloolefin may be in the gas or liquid state (including gas dissolved in a solvent). A liquid, which may or may not be a solvent for any or all of the reactants and/or products may also be present. Suitable liquids include alkanes, cycloalkanes, halogenated alkanes and cycloalkanes, ethers, water, and alcohols, except that when (III) is used, hydrocarbons should preferably be used as solvents. Specific useful solvents include methylene

chloride, hexane, CO_2 , chloroform, perfluorō(n-butyltetrahydrofuran) (herein sometimes called FC-75), toluene, dichlorobenzene, 2-ethylhexanol, and benzene.

It is particularly noteworthy that one of the liquids which can be used in this polymerization process with (II), (III), (IV) or (VII) is water, see for instance Examples 213-216. Not only can water be present but the polymerization "medium" may be largely water, and various types of surfactants may be employed so that an emulsion polymerization may be done, along with a suspension polymerization when surfactants are not employed.

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Preferred olefins and cycloolefins in the polymerization using (II), (III) or (IV) are one or more of ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-butene, cyclopentene, 1-tetradecene, and norbornene; and ethylene, propylene and cyclopentene are more preferred. Ethylene alone is especially preferred.

20 Olefinic esters or carboxylic acids of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen, hydrocarbyl, or substituted hydrocarbyl, and m is 0 or an integer of 1 to 16. It is preferred if R1 hydrocarbyl or substituted hydrocarbyl and it is more preferred if it 25 is alkyl containing 1 to 10 carbon atoms, or glycidyl. It is also preferred if m is 0 and/or R1 is alkyl containing 1 to 10 carbon atoms. It is preferred to make copolymers containing up to about 60 mole percent, preferably up to about 20 mole percent of repeat units 30 derived from the olefinic ester or carboxylic acid. Total repeat unit units in the polymer herein refer not only to those in the main chain from each monomer unit, but those in branches or side chains as well.

When using (II), (III), (IV) or (VII) as a catalyst it is preferred that R^3 and R^4 are hydrogen, methyl, or taken together are

It is also preferred that both R² and R⁵ are 2,6
diisopropylphenyl, 2,6-dimethylphenyl, 4-methylphenyl,
phenyl, 2,6-diethylphenyl, 2,4,6-trimethylphenyl and 2t-butylphenyl. When (II) is used, it is preferred that
T¹ is methyl, R⁶ is methyl or ethyl and R⁷ is methyl.
When (III) is used it is preferred that T¹ is methyl
and said Lewis base is R⁶₂O, wherein R⁶ is methyl or
ethyl. When (IV) is used it is preferred that R⁸ is
methyl, n is 3 and R¹⁶ is hydrogen. In addition in
Table II are listed all particularly preferred
combinations as catalysts for (II), (III), (IV) and

(VII).

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	Table II							
Com-	R²	R ³	R⁵	R⁵	$T^1/T^2/$	Z	M	X
pound	·				R ⁸			
Type								-
(II)	2,6-i-	Me	Me	2,6-i-	Me	OEt ₂	₽d	BAF
4	PrPh			PrPh				
(II)	2,6-i-	Н	H	2,6-i-	Me	OEt ₂	Pd	BAF
	PrPh			PrPh				
(III)	2,6-i-	Me	Me	2,6-i-	Me	OEt ₂	Ni	BAF
	PrPh			PrPh				
(III)	2,6-i-	Н	H	2,6-i-	Me	OEt ₂	Ni	BAF
	PrPh			PrPh				
(II)	2,6-	H	Н	2,6-MePh	Me	OEt ₂	₽đ	BAF
	MePh			•				
(II)	2,6-	Me	Me	2,6-MePh	Me	OEt ₂	Pd	BAF
	MePh							
(II)	2,6-i-	Me	Me	2,6-i-	Me	OEt ₂	Pd	SbFs
	PrPh			PrPh				
(II)	2,6-i-	Me	Me	2,6-i-	Me	OEt ₂	Pd	BF ₄
	PrPh			PrPh				
(II)	2,6-1-	Me	Me	2,6-i-	Me	OEt ₂	Pd	PF ₆
	PrPh			PrPh				
(II)	2,6-i-	Н	H	2,6-i-	Me	OEt ₂	₽d	SbF_{6}
	PrPh		-	PrPh	•			
(II)	2,4,6-	Me .	Me	2,4,6-	Me	OEt _?	₽đ	SbF_{ϵ}
	MePh			MePh				
(II)	2,6-i-	An	An	2,6-i-	Me	OEt ₂	Pd	SbF_{ϵ}
	PrPh			PrPh				
(II)	2,6-i-	Me	Me	2,6-i-	Me	NCMe	Pd	SbFs
	PrPh			PrPh				
(II)	Ph	Me	Me	Ph	Me	NCMe	Pđ	SbF ₆
(II)	2,6-	Me	Me	2,6-EtPh	Me	NCMe	Pd	BAF
	EtPh							
(II)	2,6-	.Me	Me	2,6-EtPh	Me	NCMe	Pd	SbF ₆
•	EtPh							
(II)	2-t-	Me	Me	2-t-BuPh	Me	NCMe	Pd	SbF_{6}
	BuPh							

(II)	1-Np	Me	Me	1-Np	Me	NCMe	Pd	SbF_6
(II)	Ph ₂ CH	Н	Н	Ph ₂ CH	Me	NCMe	Pd	SbF ₆
(II)	2-PhPh	Me	Me	2-PhPh	Me	NCMe	·Pd	· SbF ₆
(II)	Ph	a	a	Ph	Me	NCMe	Pd	BAF
(IV)	2,6-i-	Me	Me	2,6-i-	Me	Þ	Pd	\mathtt{SbF}_{6}
	PrPh.			PrPh				
(IV)	2,6-i-	Me	Me	2,6-i-	Me	b	Pd	BAF
	PrPh	•		PrPh			·	
(IV)	2,6-i-	H	. H	2,6-i-	Me	b	Pd	SbF ₆
	PrPh			PrPh				
(IV)	2,6-i-	Me	Me	2,6-i-	Me	ь	Pd	B (C ₆
	PrPh			PrPh				F ₅) ₃ C
							•	1
(II)	Ph	Me	Me	Ph	Me	NCMe	Pđ	SbF_6
(VII)	2,6-i-	Me	Me	2,6-i-	Me	<u>-</u> ·	Pd	OTf
	PrPh			PrPh	-			
(II)	Ph	Ph	Ph	Ph	Me	NCMe	Pd	BAF
(II)	Ph_2CH		Н	Ph₂CH	Me	NCMe	Pd	SbF ₆
a This group is -CMe ₂ CH ₂ CMe ₂ -								

a This group is -CMe2CH2CMe2-

When using (II), (III), (IV) or (VII) the temperature at which the polymerization is carried out is about -100°C to about +200°C, preferably about 0°C to about 150°C, more preferably about 25°C to about 100°C. The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range. The pressure can affect the microstructure of the polyolefin produced (see below).

Catalysts of the formulas (II), (III), (IV) and (VII) may also be supported on a solid catalyst (as opposed to just being added as a solid or in solution), for instance on silica gel (see Example 98). By supported is meant that the catalyst may simply be carried physically on the surface of the solid support, may be adsorbed, or carried by the support by other means.

b This group is - (CH₂)₃CO₂Me

When using (XXX) as a ligand or in any process or reaction herein it is preferred that n is 2, all of R^{30} , R^{28} and R^{29} are hydrogen, and both of R^{44} and R^{45} are 9-anthracenyl.

Another polymerization process comprises contacting a compound of the formula $[Pd(R^{13}CN)_4]X_2$ or a combination of $Pd[OC(O)R^{40}]_2$ and HX, with a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, 15 substituted norbornene and norbornene, wherein: R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R3 and R4 are each independently hydrogen, 20 hydrocarbyl, substituted hydrocarbyl or R² and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring; each \mathbb{R}^{1} is independently hydrocarbyl or substituted hydrocarbyl provided that R17 contains no olefinic bonds; R10 is 25 hydrocarbyl or substituted hydrocarbyl; and X is a weakly coordinating anion; provided that when norbornene or substituted norbornene is present no other monomer is present.

It is believed that in this process a catalyst similar to (II) may be initially generated, and this then causes the polymerization. Therefore, all of the conditions, monomers (including clefinic esters and

carboxylic acids), etc., which are applicable to the process using (II) as a polymerization catalyst are applicable to this process. All preferred items are also the same, including appropriate groups such as R², R³, R⁴, R⁵, and combinations thereof. This process however should be run so that all of the ingredients can contact each other, preferably in a single phase. Initially at least, it is preferred that this is done in solution. The molar ratio of (VIII) to palladium compound used is not critical, but for most economical use of the compounds, a moderate excess, about 25 to 100% excess, of (VIII) is preferably used.

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As mentioned above, it is believed that in the polymerization using (VIII) and $[Pd(R^{13}CN)_4]X_2$ or a Pd[II] carboxylate a catalyst similar to (II) is 15 formed. Other combinations of starting materials that can combine into catalysts similar to (II), (III), (IV) and (VII) often also cause similar polymerizations, see for instance Examples 238 and 239. Also combinations of α -diimines or other diimino 20 ligands described herein with: a nickel [0] or nickel [I] compound, oxygen, an alkyl aluminum compound and an olefin; a nickel [0] or nickel [I] compound, an acid such as HX and an olefin; or an α -diimine Ni[0] or nickel [I] complex, oxygen, an alkyl aluminum compound 25 Thus active catalysts from α -diimines and an olefin. and other bidentate imino compounds can be formed beforehand or in the same "pot" (in situ) in which the polymerization takes place. In all of the polymerizations in which the catalysts are formed in 30 situ, preferred groups on the α -diimines are the same as for the preformed catalysts.

In general Ni[0], Ni[I] or Ni(II) compounds may be used as precursors to active catalyst species. They must have ligands which can be displaced by the appropriate bidentate nitrogen ligand, or must already contain such a bidentate ligand already bound to the nickel atom. Ligands which may be displaced include

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1,5-cyclooctadiene and tris(o-tolyl)phosphite, which may be present in Ni[0] compounds, or dibenzylideneacetone, as in the useful Pd[0] precursor tris(dibenzylideneacetone)dipalladium[0]. These lower valence nickel compounds are believed to be converted into active Ni[II] catalytic species. As such they must also be contacted (react with) with an oxidizing agent and a source of a weakly coordinating anion (X). Oxidizing agents include oxygen, HX (wherein X is a weakly coordinating anion), and other well known oxidizing agents. Sources of X include HX, alkylaluminum compounds, alkali metal and silver salts of X. As can be seen above, some compounds such as HX may act as both an oxidizing agent and a source of X'. Compounds containing other lower valent metals may be converted into active catalyst species by similar methods.

When contacted with an alkyl aluminum compound or HX useful Ni[0] compounds include

R³
Ni COD
R⁴ R^{5} R^{5} R^{4} R^{5} R^{5} R^{2} R^{5} R^{5} R^{5} R^{5} R^{5} R^{7} $R^{$

Various types of Ni[0] compounds are known in the literature. Below are listed references for the types shown immediately above.

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- (XXXIII) G. van Koten, et al., Adv.
 Organometal. Chem., vol. 21, p. 151-239 (1982).
- (XXXXII) W. Bonrath, et al., Angew. Chem. Int. Ed. Engl., vol. 29, p. 298-300 (1990).
- (XXXXIV) H. tom Dieck, et al., Z.

 Natruforsch., vol. 366, p. 823-832 (1981); and M.

 Svoboda, et al., J. Organometal. Chem., vol. 191, p.

 321-328 (1980).
 - (XXXXV) G. van Koten, et al., Adv.
- 10 Organometal. Chem., vol. 21, p. 151-239 (1982).

In polymerizations using (XIV), the same preferred monomers and groups (such as R^2 , R^3 , R^4 , R^5 and X) as are preferred for the polymerization using (II) are used and preferred. Likewise, the conditions used and preferred for polymerizations with (XIV) are similar to those used and preferred for (II), except that higher olefin pressures (when the olefin is a gas) are preferred. Preferred pressures are about 2.0 to about 20 MPa. (XIV) may be prepared by the reaction of one mole of $[Pd(R^{13}CN)_4]X_2$ with one mole of (VIII) in acetonitrile or nitromethane.

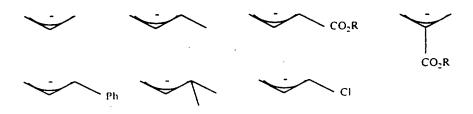
Novel compound (XIV) is used as an olefin polymerization catalyst. In preferred forms of (XIV), the preferred groups R^2 , R^3 , R^4 , R^5 and X are the same as are preferred for compound (II).

Another type of compound which is an olefin polymerization catalyst are $\pi\text{-allyl}$ and $\pi\text{-benzyl}$ compounds of the formula

XXXVII

30 wherein M is Ni(II) or Pd(II); R² and R⁵ are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen

atom has at least two carbon atoms bound to it; R^2 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; X is a weakly coordinating anion; and A is a π -allyl or π -benzyl group. By a π -allyl group is meant a monoanionic with 3 adjacent sp^2 carbon atoms bound to a metal center in an η^3 fashion. The three sp^2 carbon atoms may be substituted with other hydrocarbyl groups or functional groups. Typical π -allyl groups include



wherein R is hydrocarbyl. By a π -benzyl group is meant 5 π -allyl ligand in which two of the sp² carbon atoms are part of an aromatic ring. Typical π -benzyl groups include

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 $\pi\textsc{-Benzyl}$ compounds usually initiate polymerization of the olefins fairly readily even at room temperature, but $\pi\textsc{-allyl}$ compounds may not necessarily do so.

Initiation of π -allyl compounds can be improved by using one or more of the following methods:

- Using a higher temperature such as about 80°C.
- Decreasing the bulk of the α -dimine ligand, such as R² and R⁵ being 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl.
- Making the π -allyl ligand more bulky, such as using

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rather than the simple π -allyl group itself.

• Having a Lewis acid present while using a functional π -allyl or π -benzyl group. Relatively weak Lewis acids such a triphenylborane, tris(pentafluorophenyl)borane, and tris(3,5-trifluoromethylphenyl)borane, are preferred. Suitable functional groups include chloro and ester. "Solid" acids such as montmorillonite may also be used.

When using (XXXVII) as a polymerization catalyst, it is preferred that ethylene and/or a linear α-olefin is the monomer, or cyclopentene, more preferred if the monomer is ethylene and/or propylene, and ethylene is especially preferred. A preferred temperature for the polymerization process using (XXXVII) is about +20°C to about 100°C. It is also preferred that the partial pressure due to ethylene or propylene monomer is at least about 600 kPa.It is also noted that (XXXVII) is a novel compound, and preferred items for (XXXVII) for the polymerization process are also preferred for the compound itself.

Another catalyst for the polymerization of olefins is a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein: R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R3 and Rⁱ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; R⁵⁴ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each R⁵⁵ is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; W is alkylene or substituted alkylene containing 2 or more carbon atoms; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula R¹⁷CH=CHR¹⁷; each R¹⁷ is independently alkyl or substituted alkyl; and X is a weakly coordinating anion. It is preferred that in compound (XXXVIII) that: R⁵⁴ is phenyl or substituted phenyl, and preferred substituents are alkyl groups; each R55 is independently hydrogen or alkyl containing 1 to 10 carbon atoms; W contains 2 carbon atoms between the phenyl ring and metal atom it is bonded to or W is a divalent polymeric group derived from the polymerization of R17CH=CHR17, and it is especially preferred that it is $-CH(CH_3)CH_2-$ or $-C(CH_3)_2CH_2-$; and Z is a dialkyl ether or an olefin of the formula

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R¹⁷CH=CHR¹⁷; and combinations thereof. W is an alkylene group in which each of the two free valencies are to different carbon atoms of the alkylene group.

When W is a divalent group formed by the polymerization of R¹⁷CH=CHR¹⁷, and Z is R¹⁷CH=CHR¹⁷, the compound (XXXVIII) is believed to be a living ended polymer. That end of W bound to the phenyl ring actually is the original fragment from R⁵⁶ from which the "bridge" W originally formed, and the remaining part of W is formed from the olefin(s) R¹⁷CH=CHR¹⁷. In a sense this compound is similar in function to compound (VI).

By substituted phenyl in (XXXVIII) and (XXXIX) is meant the phenyl ring can be substituted with any grouping which does not interfere with the compound's stability or any of the reactions the compound undergoes. Preferred substituents in substituted phenyl are alkyl groups, preferably containing 1 to 10 carbon atoms.

Preferred monomers for this polymerization are ethylene and linear α -olefins, or cyclopentene, particularly propylene, and ethylene and propylene or both are more preferred, and ethylene is especially preferred.

It is noted that (XXXVIII) is a novel compound, and preferred compounds and groupings are the same as in the polymerization process.

Compound (XXXVIII) can be made by heating compound (XXXIX),

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wherein: R3 and R4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R' taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; R54 is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; each R55 is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; R56 is alkyl containing 2 to 30 carbon atoms; T3 is alkyl; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6; and X is a weakly coordinating anion. Preferred groups are the same as those in (XXXVIII). In addition it is preferred that T⁵ contain 1 to 10 carbon atoms, and more preferred that it is methyl. A preferred temperature for the conversion of (XXXIX) to (XXXVIII) is about -30°C to about 50°C. Typically the reaction takes about 10 min. to about 5 days, the higher the temperature, the faster the reaction. Another factor which affects the reaction rate is the nature of Z. The weaker the Lewis basicity of Z, the faster the desired reaction will be.

When (II), (III), (IV), (V), (VII), (VIII) or a combination of compounds that will generate similar compounds, (subject to the conditions described above) is used in the polymerization of olefins, cyclolefins, and optionally olefinic esters or carboxylic acids, polymer having what is believed to be similar to a "living end" is formed. This molecule is that from which the polymer grows to its eventual molecular weight. This compound may have the structure

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wherein: M is Ni(II) or Pd(II); R2 and R5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R3 and R4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; each R11 is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$; T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵(C=O)-, R¹⁵O(C=O)-, or -CH₂CH₂CO₂R⁸; R¹⁵ is hydrocarbyl not containing olefinic or acetylenic unsaturation; P is a divalent 15 group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when M is Pd(II), optionally one or 20 more compounds of the formula $CH_2=CH(CH_2)_mCO_2R^1$; R^8 is hydrocarbyl; each R17 is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at 25 least two saturated carbon atoms; m is 0 or an integer from 1 to 16; R1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms; and X is a weakly coordinating anion; and that when M is Ni(II), R^{11} is not $-CO_2R^8$ and when M is Pd a diene is not present. By an "olefinic ester or carboxylic acid" is meant a compound of the formula

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 $CH_2=CH(CH_2)_mCO_2R^1$, wherein m and R^1 are as defined immediately above.

This molecule will react with additional monomer (olefin, cyclic olefin, olefinic ester or olefinic carboxylic acid) to cause further polymerization. In other words, the additional monomer will be added to P, extending the length of the polymer chain. Thus P may be of any size, from one "repeat unit" to many repeat units, and when the polymerization is over and P is removed from M, as by hydrolysis, P is essentially the polymer product of the polymerization. Polymerizations with (VI), that is contact of additional monomer with this molecule takes place under the same conditions as described above for the polymerization process using (II), (III), (IV), (V), (VII) or (VIII), or combinations of compounds that will generate similar molecules, and where appropriate preferred conditions and structures are the same.

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The group T^3 in (VI) was originally the group \overline{T}^1 in (II) or (III), or the group which included R^{8} in (IV). It in essence will normally be one of the end groups of the eventual polymer product. The olefinic group which is coordinated to M, $R^{11}CH=CHR^{11}$ is normally one of the monomers, olefin, cyclic olefin, or, if Pd(II) is M, an olefinic ester or carboxylic acid. 'If more than one of these monomers is present in the reaction, it may be any one of them. It is preferred that T^2 is alkyl and especially preferred that it is methyl, and it is also preferred that R^{11} is hydrogen or n-alkyl. It is also preferred that M is Pd(II). 30

Another "form" for the living end is (XVI).

$$\begin{array}{c|cccc}
R^{3} & R^{2} \\
N & (Q)_{y} & H \\
\hline
M & C-R^{1} \\
N & H-C-R^{1} \\
R^{5} & PT^{3}
\end{array}$$
(XVI) (X)_a

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This type of compound is sometimes referred to as a compound in the "agostic state". In fact both (VI) and (XVI) may coexist together in the same polymerization, both types of compound representing living ends. It is believed that (XVI)-type compounds are particularly favored when the end of the growing polymer chain bound to the transition metal is derived from a cyclic olefin such as cyclopentene. Expressed in terms of the structure of (XVI) this is when both of R¹¹ are hydrocarbylene to form a carbocyclic ring, and it is preferred that this be a five-membered carbocyclic ring.

For both the polymerization process using (XVI) and the structure of (XVI) itself, the same conditions and groups as are used and preferred for (VI) are also used and preferred for (XVI), with the exception that for \mathbb{R}^{11} it is preferred in (XVI) that both of \mathbb{R}^{11} are hydrocarbylene to form a carbocyclic ring.

This invention also concerns a compound of the formula

wherein: M is Ni(II) or Pd(II); R² and R⁵ are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a

ring; each R^{14} is independently hydrogen, alkyl or [when M is Pd(II)] $-(CH_2)_mCO_2R^1$; R^1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms; T^4 is alkyl, $-R^{60}C(0)OR^8$, $R^{15}(C=0)$ or $R^{15}OC(=0)$ -; R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds; R^{60} is alkylene not containing olefinic or acetylenic bonds; R^8 is hydrocarbyl; and X is a weakly coordinating anion.

(IX) may also be used to polymerize olefins, cyclic olefins, and optionally olefinic esters and carboxylic acids. The same conditions (except as noted below) apply to the polymerizations using (IX) as they do for (VI). It is preferred that M is Pd(II) and T⁴ is methyl.

15 A compound of formula (V) may also be used as a catalyst for the polymerization of olefins, cyclic olefins, and optionally olefinic esters and/or carboxylic acids. In this process (V) is contacted with one or more of the essential monomers. Optionally 20 a source of a relatively weakly coordinating anion may also be present. Such a source could be an alkali metal salt of BAF or AgX (wherein X is the anion), etc. Preferably about 1 mole of the source of X, such as AgX, will be added per mole of (V). This will usually be done in the liquid phase, preferably in which (V) and the source of the anion are at least partially soluble. The conditions of this polymerization are otherwise the same as described above for (II); (III), (IV) and (VII), including the preferred conditions and 30 ingredients.

In polymerizations using (XX) as the catalyst, a first compound which is a source of a relatively noncoordinating monoanion is present. Such a source can be an alkali metal or silver salt of the monoanion.

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It is preferred that the alkali metal cation is sodium or potassium. It is preferred that the monoanion is SbF₆, BAF, PF₆, or BF₄, and more preferred that it is BAF. It is preferred that T1 is methyl and/or S is chlorine. All other preferred groups and conditions for these polymerizations are the same as for polymerizations with (II).

In all of the above polymerizations, and the catalysts for making them it is preferred that R2 and R^5 , if present, are 2,6-diisopropylphenyl and R^3 and R^4 are hydrogen or methyl. When cyclopentene is polymerized, is preferred that R² and R⁵ (if present) are 2,6-dimethylphenyl or 2,4,6-trimethylphenyl and that R^3 and R^4 taken together are An. R^2 , R^3 , R^4 and R^5 and other groups herein may also be substituted hydrocarbyl. As previously defined, the substituent groups in substituted hydrocarbyl groups (there may be 20 one or more substituent groups) should not substantially interfere with the polymerization or other reactions that the compound is undergoing. Whether a particular group will interfere can first be judged from the artisans general knowledge and the particular polymerization or other reaction that is involved. For instance, in polymerizations where an alkyl aluminum compound is used may not be compatible with the presence of groups containing an active (relatively acidic) hydrogen atom, such as hydroxyl or 30 carboxyl because of the known reaction of alkyl aluminum compounds with such active hydrogen containing groups (but such polymerizations may be possible if

enough "extra" alkyl aluminum compound is added to react with these groups). However, in very similar polymerizations where alkyl aluminum compounds are not present, these groups containing active hydrogen may be present. Indeed many of the polymerization processes described herein are remarkably tolerant to the presence of various functional groups. Probably the most important considerations as to the operability of compounds containing any particular functional group are the effect of the group on the coordination of the 10 metal atom (if present), and side reaction of the group with other process ingredients (such as noted above). Therefore of course, the further away from the metal atom the functional group is, the less likely it is to influence, say, a polymerization. If there is doubt as 15 to whether a particular functional group, in a particular position, will affect a reaction, simple minimal experimentation will provide the requisite answer. Functional groups which may be present in R2, R³, R⁴, R⁵, and other similar radicals herein include 20 hydroxy, halo (fluoro, chloro, bromo and iodo), ether, ester, dialkylamino, carboxy, oxo (keto and aldehyo), nitro, amide, thioether, and imino. Preferred functional groups are hydroxy, halo, ether and 25 dialkylamino.

Also in all of the polymerizations, the (cyclo)olefin may be substituted hydrocarbyl. Suitable substituents include ether, keto, aldehyde, ester, carboxylic acid.

In all of the above polymerizations, with the exceptions noted below, the following monomer(s), to produce the corresponding homo- or copolymers, are preferred to be used: ethylene; propylene; ethylene and propylene; ethylene and an α -olefin; an α -olefin; ethylene and an alkyl acrylate, especially methyl acrylate; ethylene and acrylic acid; ethylene and carbon monoxide; ethylene, and carbon monoxide and an acrylate ester or acrylic acid, especially methyl

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acrylate; propylene and alkyl acrylate, especially methyl acrylate; cyclopentene; cyclopentene and ethylene; cyclopentene and propylene. Monomers which contain a carbonyl group, including esters, carboxylic acids, carbon monoxide, vinyl ketones, etc., can be polymerized with Pd(II) containing catalysts herein, with the exception of those that require the presence of a neutral or cationic Lewis acid or cationic Bronsted acid, which is usually called the "first compound" in claims describing such polymerization processes.

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Another useful "monomer" for these polymerization processes is a C4 refinery catalytic cracker stream, which will often contain a mixture of n-butane, isobutane, isobutene, 1-butene, 2-butenes and small 15 amounts of butadiene. This type of stream is referred to herein as a "crude butenes stream". may act as both the monomer source and "solvent" for the polymerization. It is preferred that the concentration of 1- and 2-butenes in the stream be as 20 high as possible, since these are the preferred compounds to be polymerized. The butadiene content should be minimized because it may be a polymerization catalyst poison. The isobutene may have been previously removed for other uses. After being used in the polymerization (during which much or most of the 1butene would have been polymerized), the butenes stream can be returned to the refinery for further processing.

In many of the these polymerizations certain general trends may be noted, although for all of these trends there are exceptions. These trends (and exceptions) can be gleaned from the Examples.

pressure of the monomers (especially gaseous monomers such as ethylene) has an effect on the polymerizations in many instances. Higher pressure often affects the polymer microstructure by reducing branching, especially in ethylene containing polymers. This effect is more pronounced for Ni catalysts than Pd

catalysts. Under certain conditions higher pressures also seem to give higher productivities and higher molecular weight. When an acrylate is present and a Pd catalyst is used, increasing pressure seems to decrease the acrylate content in the resulting copolymer.

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Temperature also affects these polymerizations. Higher temperature usually increases branching with Ni catalysts, but often has little such effect using Pd catalysts. With Ni catalysts, higher temperatures appear to often decrease molecular weight. With Pd catalysts, when acrylates are present, increasing temperature usually increases the acrylate content of the polymer, but also often decreases the productivity and molecular weight of the polymer.

Anions surprisingly also often affect molecular 15 weight of the polymer formed. More highly coordinating anions often give lower molecular weight polymers. Although all of the anions useful herein are relatively weakly coordinating, some are more strongly coordinating than others. The coordinating ability of 20. such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. The results found 25 herein in which the molecular weight of the polymer produced is related to the coordinating ability of the anion used, is in line with the coordinating abilities of these anions as described in Beck (p. 1411) and Strauss (p. 932, Table II). 30

In addition to the "traditional" weakly coordinating anions cited in the paragraph immediately above, heterogeneous anions may also be employed. In these cases, the true nature of the counterion is poorly defined or unknown. Included in this group are MAO, MMAO and related aluminoxanes which do not form true solutions. The resulting counterions are thought to bear anionic aluminate moieties related to those

cited in the paragraph immediately above. Polymeric anionic materials such as Nafion" polyfluorosulfonic acid can function as non-coordinating counterions. In addition, a wide variety of heterogeneous inorganic 5 materials can be made to function as non-coordinating counterions. Examples would include aluminas, silicas, silica/aluminas, cordierites, clays, MgCl₂, and many others utilized as traditional supports for Ziegler-Natta olefin polymerization catalysts. These are generally materials which have Lewis or Bronsted 10 acidity. High surface area is usually desired and often these materials will have been activated through some heating process. Heating may remove excess surface water and change the surface acidity from Bronsted to Lewis type. Materials which are not active 15 in the role may often be made active by surface treatment. For instance, a surface-hydrated silica, zinc oxide or carbon can be treated with an organoaluminum compound to provide the required 20 functionality.

The catalysts described herein can be heterogenized through a variety of means. heterogeneous anions in the paragraph immediately above will all serve to heterogenize the catalysts. Catalysts can also be heterogenized by exposing them to 25 small quantities of a monomer to encapsulate them in a polymeric material through which additional monomers will diffuse. Another method is to spray-dry the catalyst with its suitable non-coordinating counterion onto a polymeric support. Heterogeneous versions of 30 the catalyst are particularly useful for running gasphase polymerizations. The catalyst is suitably diluted and dispersed on the surface of the catalyst support to control the heat of polymerization. When applied to fluidized-bed polymerizations, the heterogeneous supports provide a convenient means of

catalyst introduction.

Anions have been found to have another unexpected effect. They can effect the amount of incorporation of an acrylic monomer such as an ester into an olefin/acrylic copolymer. For instance it has been found that SbF_6 anion incorporates more fluorinated alkyl acrylate ester into an ethylene copolymer than BAF anion, see for instance Example 302.

Another item may effect the incorporation of polar monomers such as acrylic esters in olefin copolymers. 10 It has been found that catalysts containing less bulky α -diimines incorporate more of the polar monomer into the polymer (one obtains a polymer with a higher percentage of polar monomer) than a catalyst containing a more bulky α -diimine, particularly when ethylene is the olefin comonomer. For instance, in an α -diimine of 15 formula (VIII), if R² and R⁵ are 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl, more acrylic monomer will be incorporated into the polymer. However, another common effect of using a less bulky catalyst is to produce a polymer with lower molecular weight. 20 Therefore one may have to make a compromise between polar monomer content in the polymer and polymer molecular weight.

When an olefinic carboxylic acid is polymerized into the polymer, the polymer will of course contain carboxyl groups. Similarly in an ester containing polymer, some or all of the ester groups may be hydrolyzed to carboxyl groups (and vice versa). The carboxyl groups may be partially or completely converted into salts such as metallic salts. Such polymeric salts are termed ionomers. Ionomers are useful in adhesives, as ionomeric elastomers, and as molding resins. Salts may be made with ions of metals such as Na, K, Zn, Mg, Al, etc. The polymeric salts may be made by methods known to the artisan, for instance reaction of the carboxylic acid containing polymers with various compounds of the metals such as bases (hydroxides, carbonates, etc.) or other

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compounds, such as acetylacetonates. Novel polymers that contain carboxylic acid groups herein, also form novel ionomers when the carboxylic acid groups are partially or fully converted to carboxylate salts.

When copolymers of an olefinic carboxylic acid or olefinic ester and selected olefins are made, they may be crosslinked by various methods known in the art, depending on the specific monomers used to make the polymer. For instance, carboxyl or ester containing polymers may be crosslinked by reaction with diamines to form bisamides. Certain functional groups which may be present on the polymer may be induced to react to crosslink the polymer. For instance epoxy groups (which may be present as glycidyl esters) may be crosslinked by reaction of the epoxy groups, see for instance Example 135.

It has also been found that certain fluorinated olefins, some of them containing other functional groups may be polymerized by nickel and palladium catalysts. Note that these fluorinated olefins are 20 included within the definition of $H_2C=CHR^{17}$, wherein R^{17} can be considered to be substituted hydrocarbyl, the substitution being fluorine and possibly other substituents. Olefins which may be polymerized include $H_2C=CH(CH_2)_aR_fR^{42}$ wherein a is an integer of 2 to 20, R_f is perfluoroalkylene optionally containing one or more ether groups, and R42 is fluorine or a functional group. Suitable functional groups include hydrogen, chlorine, bromine or iodine, ester, sulfonic acid (-SO3H), and sulfonyl halide. Preferred groups for R42 include fluorine, ester, sulfonic acid, and sulfonyl fluoride. A sulfonic acid group containing monomer does not have to be polymerized directly. preferably made by hydrolysis of a sulfonyl halide group already present in an already made polymer. It is preferred that the perfluoroalkylene group contain 2 to 20 carbon atoms and preferred perfluoroalkylene groups are $-(CF_2)_b$ - wherein b is 2 to 20, and -

 $(CF_2)_dOCF_2CF_2$ - wherein d is 2 to 20. A preferred olefinic comonomer is ethylene or a linear α -olefin, and ethylene is especially preferred. Polymerizations may be carried out with many of the catalysts described herein, see Examples 284 to 293.

As described herein, the resulting fluorinated polymers often don't contain the expected amount of branching, and/or the lengths of the branches present are not those expected for a simple vinyl polymerization.

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The resulting polymers may be useful for compatibilizing fluorinated and nonfluorinated polymers, for changing the surface characteristics of fluorinated or nonfluorinated polymers (by being mixed with them), as molding resins, etc. Those polymers 15 containing functional groups may be useful where those functional groups may react or be catalysts. For instance, if a polymer is made with a sulfonyl fluoride group (R42 is sulfonyl fluoride) that group may be hydrolyzed to a sulfonic acid, which being highly 20 fluorinated is well known to be a very strong acid. Thus the polymer may be used as an acid catalyst, for example for the polymerization of cyclic ethers such as tetrahydrofuran.

In this use it has been found that this polymer is more effective than a completely fluorinated sulfonic acid containing polymer. For such uses the sulfonic acid content need not be high, say only 1 to 20 mole percent, preferably about 2 to 10 mole percent of the repeat units in the polymer having sulfonic acid groups. The polymer may be crosslinked, in which case it may be soluble in the medium (for instance tetrahydrofuran), or it may be crosslinked so it swollen but not dissolved by the medium, Or it may be coated onto a substrate and optionally chemically attached and/or crosslinked, so it may easily be separated from the other process ingredients.

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One of the monomers that may be polymerized by the above catalysts is ethylene (E), either by itself to form a homopolymer, or with α -olefins and/or olefinic esters or carboxylic acids. The structure of the polymer may be unique in terms of several measurable properties.

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These polymers, and others herein, can have unique structures in terms of the branching in the polymer. Branching may be determined by NMR spectroscopy (see the Examples for details), and this analysis can 10 determine the total number of branches, and to some extent the length of the branches. Herein the amount of branching is expressed as the number of branches per 1000 of the total methylene (-CH2-) groups in the polymer, with one exception. Methylene groups that are 15 in an ester grouping, i.e. $-CO_2R$, are not counted as part of the 1000 methylenes. These methylene groups include those in the main chain and in the branches. These polymers, which are E homopolymers, have a branch content of about 80 to about 150 branches per 1000 20 methylene groups, preferably about 100 to about 130 branches per 1000 methylene groups. These branches do not include polymer end groups. In addition the distribution of the sizes (lengths) of the branches is unique. Of the above total branches, for every 100 25 that are methyl, about 30 to about 90 are ethyl, about 4 to about 20 are propyl, about 15 to about 50 butyl, about 3 to about 15 are amyl, and about 30 to about 140 are hexyl or longer, and it is preferred that for every 100 that are methyl; about 50 to about 75 are ethyl, 30 about 5 to about 15 are propyl, about 24 to about 40 are butyl, about 5 to 10 are amyl, and about 65 to about 120 are hexyl or larger. These E homopolymers are often amorphous, although in some there may be a small amount of crystallinity. 35

Another polyolefin, which is an E homopolymer that can be made by these catalysts has about 20 to about 150 branches per 1000 methylene groups, and, per 100

methyl groups, about 4 to about 20 ethyl groups, about 1 to about 12 propyl groups, about 1 to about 12 butyl group, about 1 to about 10 amyl groups, and 0 to about 20 hexyl or larger groups. Preferably this polymer has about 40 to about 100 methyl groups per 1000 methylene groups, and per 100 methyl groups, about 6 to about 15 ethyl groups, about 2 to about 10 propyl groups, about 2 to about 10 butyl groups, about 2 to about 8 amyl groups, and about 2 to about 15 hexyl or larger groups.

Many of the polyolefins herein, including homopolyethylenes, may be crosslinked by various methods known in the art, for instance by the use of peroxide or other radical generating species which can crosslink these polymers. Such crosslinked polymers are novel when the uncrosslinked polymers from which they are derived are novel, because for the most part the structural feature(s) of the uncrosslinked polymers which make them novel will be carried over into the crosslinked forms.

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In addition, some of the E homopolymers have an exceptionally low density, less than about 0.86 g/mL, preferably about 0.85 g/mL or less, measured at 25°C. This density is based on solid polymer.

Homopolymers of polypropylene (P) can also have unusual structures. Similar effects have been observed with other α -olefins (e.g. 1-hexene). A "normal" P homopolymer will have one methyl group for each methylene group (or 1000 methyl groups per 1000 methylene groups), since the normal repeat unit is - CH(CH₃)CH₂-. However, using a catalyst of formula (I) in which M is Ni(II) in combination with an alkyl aluminum compound it is possible to produce a P homopolymer with about 400 to about 600 methyl groups per 1000 methylene groups, preferably about 450 to about 550 methyl groups per 1000 methylene groups. Similar effects have been observed with other α -olefins (e.g. 1-hexene).

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In the polymerization processes described herein olefinic esters and/or carboxylic acids may also be present, and of course become part of the copolymer formed. These esters may be copolymerized with one or more of E and one or more α-olefins. When copolymerized with E alone polymers with unique structures may be formed.

In many such E/olefinic ester and/or carboxylic acid copolymers the overall branching level and the distribution of branches of various sizes are unusual. In addition, where and how the esters or carboxylic acids occur in the polymer is also unusual. A relatively high proportion of the repeat units derived from the olefinic esters are at the ends of branches. In such copolymers, it is preferred that the repeat units derived from the olefinic esters and carboxylic acids are about 0.1 to 40 mole percent of the total repeat units, more preferably about 1 to about 20 mole percent. In a preferred ester, m is 0 and R1 is hydrocarbyl or substituted hydrocarbyl. preferred that R1 is alkyl containing 1 to 20 carbon atoms, more preferred that it contains 1 to 4 carbon atoms, and especially preferred that R1 is methyl.

One such preferred dipolymer has about 60 to 100 methyl groups (excluding methyl groups which are esters) per 1000 methylene groups in the polymer, and contains, per 100 methyl branches, about 45 to about 65 ethyl branches, about 1 to about 3 propyl branches, about 3 to about 10 butyl branches, about 1 to about 3 amyl branches, and about 15 to about 25 hexyl or longer branches. In addition, the ester and carboxylic acid containing repeat units are often distributed mostly at the ends of the branches as follows. If the branches, and the carbon atom to which they are attached to the main chain, are of the formula -CH(CH₂)_nCO₂R¹, wherein the CH is part of the main chain, then in some of these polymers about 40 to about 50 mole percent of ester groups are found in branches where n is 5 or more,

about 10 to about 20 mole percent when n is 4, about 20 to 30 mole percent when n is 1, 2 and 3 and about 5 to about 15 mole percent when n is 0. When n is 0, an acrylate ester has polymerized "normally" as part of the main chain, with the repeat unit -CH₂-CHCO₂R¹-.

These branched polymers which contain olefin and olefinic ester monomer units, particularly copolymers of ethylene and methyl acrylate and/or other acrylic esters are particularly useful as viscosity modifiers for lubricating oils, particularly automotive lubricating oils.

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Under certain polymerization conditions, some of the polymerization catalysts described herein produce polymers whose structure is unusual, especially considering from what compounds (monomers) the polymers 15 were made, and the fact that polymerization catalysts used herein are so-called transition metal coordination catalysts (more than one compound may be involved in the catalyst system, one of which must include a transition metal). Some of these polymers were 20 described in a somewhat different way above, and they may be described as "polyolefins" even though they may contain other monomer units which are not olefins (e.g., olefinic esters). In the polymerization of an unsaturated compound of the formula H2C=CH(CH2)eG, wherein e is 0 or an integer of 1 or more, and G is hydrogen or -CO₂R¹, the usual ("normal") polymeric repeat unit obtained would be -CH2-CH[(CH2)eG]-, wherein the branch has the formula - (CH2) G. However, with some of the instant catalysts a polymeric unit may be -CH2-30 $CH[(CH_2)_fG]$ -, wherein $f \neq e$, and f is 0 or an integer of 1 or more. If f<e, the "extra" methylene groups may If f>e (parts of) be part of the main polymer chain. additional monomer molecules may be incorporated into that branch. In other words, the structure of any 35 polymeric unit may be irregular and different for monomer molecules incorporated into the polymer, and the structure of such a polymeric unit obtained could

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be rationalized as the result of "migration of the active polymerizing site" up and down the polymer chain, although this may not be the actual mechanism. This is highly unusual, particularly for polymerizations employing transition metal coordination catalysts.

For "normal" polymerizations, wherein the polymeric unit -CH₂-CH[(CH₂)_eG]- is obtained, the theoretical amount of branching, as measured by the number of branches per 1000 methylene (-CH₂-) groups can be calculated as follows which defines terms "theoretical branches" or "theoretical branching" herein:

Theoretical branches = 1000*Total mole fraction of α -olefins $\{ [\Sigma(2\text{-mole fraction e=0})] + [\Sigma(\text{mole fraction } \alpha\text{-olefinee})] \}$

In this equation, an α -olefin is any olefinic compound $H_2C=CH(CH_2)_eG$ wherein $e\neq 0$. Ethylene or an acrylic compound are the cases wherein e=0. Thus to calculate the number of theoretical branches in a polymer made from 50 mole percent ethylene (e=0), 30 mole percent propylene (e=1) and 20 mole percent methyl 5-heptenoate (e=4) would be as follows:

Theoretical branches = 1000=0.5 = 238 (branches/1000 methylenes).

{[(2=0.5)]+{(0.30=1)+(0.20=4)}}

The "1000 methylenes" include all of the methylene groups in the polymer, including methylene groups in the branches.

For some of the polymerizations described herein, the actual amount of branching present in the polymer is considerably greater than or less than the above theoretical branching calculations would indicate. For instance, when an ethylene homopolymer is made, there should be no branches, yet there are often many such branches. When an α -olefin is polymerized, the

branching level may be much lower or higher than the theoretical branching level. It is preferred that the actual branching level is at 90% or less of the theoretical branching level, more preferably about 80% or less of the theoretical branching level, or 110% or more of the theoretical branching level, more preferably about 120% or more of the theoretical branching level. The polymer should also have at least about 50 branches per 1000 methylene units, preferably about 75 branches per 1000 methylene units, and more preferably about 100 branches per 1000 methylene units. In cases where there are "0" branches theoretically present, as in ethylene homopolymers or copolymers with acrylics, excess branches as a percentage cannot be calculated. In that instance if the polymer has 50 or more, preferably 75 or more branches per 1000 methylene groups, it has excess branches (i.e. in branches in which f>0).

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These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

As will be understood from the above discussion, the lengths of the branches ("f") do not necessarily correspond to the original sizes of the monomers used ("e"). Indeed branch lengths are often present which do not correspond to the sizes of any of the monomers used and/or a branch length may be present "in excess". By "in excess" is meant there are more branches of a particular length present than there were monomers which corresponded to that branch length in the polymer. For instance, in the copolymerization of 75 mole percent ethylene and 25 mole percent 1-butene it would be expected that there would be 125 ethyl branches per 1000 methylene carbon atoms. If there

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were more ethyl branches than that, they would be in excess compared to the theoretical branching. There may also be a deficit of specific length branches. there were less than 125 ethyl branches per 1000 5 methylene groups in this polymer there would be a deficit. Preferred polymers have 90% or less or 110% or more of the theoretical amount of any branch length present in the polymer, and it is especially preferred if these branches are about 80% or less or about 120% or more of the theoretical amount of any branch length. In the case of the 75 mole percent ethylene/25 mole percent 1-butene polymer, the 90% would be about 113 ethyl branches or less, while the 110% would be about 138 ethyl branches or more. Such polymers may also or exclusively contain at least 50 branches per 1000 methylene atoms with lengths which should not theoretically (as described above) be present at all.

These polymers also have "at least two branches of different lengths containing less than 6 carbon atoms each." By this is meant that branches of at least two different lengths (i.e. number of carbon atoms), and containing less than 6 carbon atoms, are present in the polymer. For instance the polymer may contain ethyl and butyl branches, or methyl and amyl branches.

Some of the polymers produced herein are novel because of unusual structural features. Normally, in polymers of alpha-olefins of the formula CH2=CH(CH2)aH wherein a is an integer of 2 or more made by coordination polymerization, the most abundant, and often the only, branches present in such polymers have the structure - (CH₂)_aH. Some of the polymers produced herein are novel because methyl branches comprise about 25% to about 75% of the total branches in the polymer. Such polymers are described in Examples 139, 162, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high percentage (25-75%) of methyl branches (of the total branches present), they also contain linear branches of the

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structure $-(CH_2)_nH$ wherein n is an integer of six or greater. Such polymers are described in Examples 139, 173 and 243-245. Some of the polymers produced herein are novel because in addition to having a high percentage (25-75%) of methyl branches (of the total branches present), they also contain the structure (XXVI), preferably in amounts greater than can be accounted for by end groups, and more preferably greater than 0.5 (XXVI) groups per thousand methyl groups in the polymer greater than can be accounted for by end groups.

$$CH_3$$

 $-CH_2-CH-(CH_2)_aH$ (XXVI)

15 Normally, homo- and copolymers of one or more alpha-olefins of the formula $CH_2=CH(CH_2)_aH$ wherein a is an integer of 2 or more contain as part of the polymer backbone the structure (XXV)

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wherein \mathbb{R}^{35} and \mathbb{R}^{36} are alkyl groups. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of R^{35} and R^{36} are -(CH₂)_aH. However, in certain 25 of these polymers described herein, about 2 mole percent or more, preferably about 5 mole percent or more and more preferably about 50 mole percent or more of the total amount of (XXV) in said polymer consists of the structure where one of ${\rm R}^{35}$ and ${\rm R}^{36}$ is a methyl group and the other is an alkyl group containing two or more carbon atoms. Furthermore, in certain of these polymers described herein, structure (XXV) may occur in side chains as well as in the polymer backbone. Structure (XXV) can be detected by 13C NMR. The signal

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for the carbon atom of the methylene group between the two methine carbons in (XXV) usually occurs in the ¹³C NMR at 41.9 to 44.0 ppm when one of R³⁵ and R³⁶ is a methyl group and the other is an alkyl group containing two or more carbon atoms, while when both R³⁵ and R³⁶ contain 2 or more carbon atoms, the signal for the methylene carbon atom occurs at 39.5 to 41.9 ppm. Integration provides the relative amounts of these structures present in the polymer. If there are interfering signals from other carbon atoms in these regions, they must be subtracted from the total integrals to give correct values for structure (XXV).

Normally, homo- and copolymers of one or more alpha-olefins of the formula $CH_2=CH\left(CH_2\right)_aH$ wherein a is an integer of 2 or more (especially those made by coordination polymerization) contain as part of the polymer backbone structure (XXIV) wherein n is 0, 1, or When n is 0, this structure is termed "head to head" polymerization. When n is 1, this structure is termed "head to tail" polymerization. When n is 2, this structure is termed "tail to tail" polymerization. In most such polymers of alpha-olefins of this formula (especially those produced by coordination-type polymerizations), both of R^{37} and R^{38} are -(CH₂)_aH. However some of the polymers of alpha-olefins of this formula described herein are novel in that they also contain structure (XXIV) wherein n = a, R^{37} is a methyl group, and R38 is an alkyl group with 2 or more carbon atoms.

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Normally polyethylene made by coordination polymerization has a linear backbone with either no

branching, or small amounts of linear branches. Some of the polyethylenes described herein are unusual in that they contain structure (XXVII) which has a methine carbon that is not part of the main polymer backbone.

Normally, polypropylene made by coordination polymerization has methyl branches and few if any 10 branches of other sizes. Some of the polypropylenes described herein are unusual in that they contain one or both of the structures (XXVIII) and (XXIX).

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{CH} \\ \mathsf{CH}_2 \\ \mathsf{CH_3} \\ \mathsf{--CH----} \\ \mathsf{CH_3} \\ \mathsf{--CH_2CH_2-CH-CH_3} \\ \end{array} (XXIX)$$

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As the artisan understands, in coordination polymerization alpha-olefins of the formula $CH_2=CH(CH_2)_aH$ may insert into the growing polymer chain in a 1,2 or 2,1 manner. Normally these insertion steps lead to 1,2- enchainment or 2,1-enchainment of the monomer. Both of these fundamental steps form a - $(CH_2)_aH$ branch. However, with some catalysts herein, some of the initial product of 1,2 insertion can rearrange by migration of the coordinated metal atom to the end of the last inserted monomer before insertion of additional monomer occurs. This results in omega, 2-enchainment and the formation of a methyl branch.

It is also known that with certain other catalysts, some of the initial product of 2,1 insertion can rearrange in a similar manner by migration of the coordinated metal atom to the end of the last inserted monomer. This results in omega,1-enchainment and no branch is formed.

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Of the four types of alpha-olefin enchainment, omega,1-enchainment is unique in that it does not generate a branch. In a polymer made from an alpha-olefin of the formula $CH_2=CH(CH_2)_aH$, the total number of branches per 1000 methylene groups (B) can be expressed as:

 $B = (1000) (1-X_{\omega,1})/[(1-X_{\omega,1})a + X_{\omega,1}(a+2)]$ where $X_{\omega,1}$ is the fraction of omega,1-enchainment Solving this expression for $X_{\omega,1}$ gives: $X_{\omega,1} = (1000 - aB)/(1000 + 2B)$

This equation provides a means of calculating the fraction of omega,1-enchainment in a polymer of a linear alpha-olefin from the total branching B. Total branching can be measured by ¹H NMR or ¹³C NMR. Similar equations can be written for branched alpha-

olefins. For example, the equation for 4-methyl-1-pentene is:

 $X_{\omega,1} = (2000 - 2B)/(1000 + 2B)$

Most polymers of alpha-olefins made by other coordination polymerization methods have less than 5% omega, 1-enchainment. Some of the alpha-olefin polymers described herein have unusually large amounts (say >5%) of omega, 1-enchainment. In essence this is similar to stating that a polymer made from an α -olefin has much less than the "expected" amount of branching. Although many of the polymerizations described herein give substantial amounts of ω ,1- and other unusual forms of enchainment of olefinic monomers, it has surprisingly been found that "unsymmetrical" α -diimine ligands of formula (VIII) give especially high amounts of ω ,1-15 enchainment. In particular when R^2 and R^5 are phenyl, and one or both of these is substituted in such a way as different sized groups are present in the 2 and 6 position of the phenyl ring(s), ω ,1-enchainment is enhanced. For instance, if one or both of R^2 and R^5 20 are 2-t-butylphenyl, this enchainment is enhanced. this context when R² and/or R⁵ are "substituted" phenyl the substitution may be not only in the 2 and/or 6 positions, but on any other position in the phenyl ring. For instance, 2,5-di-t-butylphenyl, and 2-t-25 butyl-4,6-dichlorophenyl would be included in substituted phenyl.

The steric effect of various groupings has been quantified by a parameter called E_s , see R. W. Taft, Jr., J. Am. Chem. Soc., vol. 74, p. 3120-3128, and M.S. Newman, Steric Effects in Organic Chemistry, John Wiley & Sons, New York, 1956, p. 598-603. For the purposes herein, the E_s values are those for o-substituted benzoates described in these publications. If the value for E_s for any particular group is not known, it can be determined by methods described in these publications. For the purposes herein, the value of hydrogen is defined to be the same as for methyl. It

is preferred that difference in E_8 , when R^* Tand preferably also R^5) is phenyl, between the groups substituted in the 2 and 6 positions of the phenyl ring is at least 0.15, more preferably at least about 0.20, and especially preferably about 0.6 or more. These phenyl groups may be unsubstituted or substituted in any other manner in the 3, 4 or 5 positions.

These differences in E_s are preferred in a diimine such as (VIII), and in any of the polymerization processes herein wherein a metal complex containing an α -diimine ligand is used or formed. The synthesis and use of such α -diimines is illustrated in Examples 454-463.

Because of the relatively large amounts of ω ,1-enchainment that may be obtained using some of the polymerization catalysts reported herein novel polymers can be made. Among these homopolypropylene (PP). In some of the PP's made herein the structure

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$$--- C^{a}HCH_{2}CH_{2}C^{d}H_{2}(C^{b}H_{2})_{n}C^{d}H_{2}CH_{2}CH_{2}C^{a}H---$$

(XXXX)

may be found. In this structure each C^a is a methine carbon atom that is a branch point, while each C^b is a methylene group that is more than 3 carbon atoms removed from any branch point (C^a) . Herein methylene groups of the type $-C^bH_2$ - are termed δ + (or delta+) methylene groups. Methylene groups of the type $-C^dH_2$ -, which are exactly the third carbon atom from a branch point, are termed γ (gamma) methylene groups. The NMR signal for the δ + methylene groups occurs at about 29.75 ppm, while the NMR signal for the γ methylene groups appears at about 30.15 ppm. Ratios of these types of methylene groups to each other and the total number of methylene groups in the PP is done by the usual NMR integration techniques.

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It is preferred that PP's made herein have about 25 to about 300 δ + methylene groups per 1000 methylene groups (total) in the PP.

It is also preferred that the ratio of $\delta+:\gamma$ methylene groups in the PP be 0.7 to about 2.0.

The above ratios involving $\delta +$ and γ methylene groups in PP are of course due to the fact that high relatively high ω ,1 enchainment can be obtained. It is preferred that about 30 to 60 mole percent of the monomer units in PP be enchained in an ω ,1 fashion. Using the above equation, the percent ω ,1 enchainment for polypropylene can be calculated as:

 $% \omega , 1 = (100) (1000-B) / (1000+2B)$

wherein B is the total branching (number of methyl groups) per 1000 methylene groups in the polymer.

Homo- or copolymers of one or more linear $\alpha-$ olefins containing 3 to 8 carbon atoms may also have $\delta+$ carbon atoms in them, preferably at least about 1 or more $\delta+$ carbon atoms per 1000 methylene groups.

The above polymerization processes can of course 20 be used to make relatively random copolymers (except for certain CO copolymers) of various possible monomers. However, some of them can also be used to make block polymers. A block polymer is conventionally 25 defined as a polymer comprising molecules in which there is a linear arrangement of blocks, a block being a portion of a polymer molecule which the monomeric units have at least one constitutional or configurational feature absent from adjacent portions (definition from H. Mark, et al., Ed., Encyclopedia of 30 Polymer Science and Engineering, Vol. 2, John Wiley & Sons, New York, 1985, p. 324). Herein in a block copolymer, the constitutional difference is a difference in monomer units used to make that block, while in a block homopolymer the same monomer(s) are used but the repeat units making up different blocks are different structure and/or ratios of types of structures.

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Since it is believed that many of the polymerization processes herein have characteristics that often resemble those of living polymerizations, making block polymers may be relatively easy. 5 method is to simply allow monomer(s) that are being polymerized to be depleted to a low level, and then adding different monomer(s) or the same combination of This process may be monomers in different ratios. repeated to obtain polymers with many blocks.

Lower temperatures, say about less than 0°C, preferably about -10° to about -30°, tends to enhance the livingness of the polymerizations. Under these conditions narrow molecular weight distribution polymers may be obtained (see Examples 367-369 and 371), and block copolymers may also be made (Example 370).

As pointed out above, certain polymerization conditions, such as pressure, affect the microstructure of many polymers. The microstructure in turn affects 20 many polymer properties, such as crystallization. Thus, by changing polymerization conditions, such as the pressure, one can change the microstructure of the part of the polymer made under those conditions. of course leads to a block polymer, a polymer have defined portions having structures different from other defined portions. This may be done with more than one monomer to obtain a block copolymer, or may be done with a single monomer or single mixture of monomers to obtain a block homopolymer. For instance, in the polymerization of ethylene, high pressure sometimes leads to crystalline polymers, while lower pressures give amorphous polymers. Changing the pressure repeatedly could lead to an ethylene homopolymer containing blocks of amorphous polyethylene and blocks If the blocks were of the of crystalline polyethylene. correct size, and there were enough of them, a thermoplastic elastomeric homopolyethylene could be

produced. Similar polymers could possibly be made from other monomer(s), such as propylene.

Homopolymers of α -olefins such as propylene, that is polymers which were made from a monomer that consisted essentially of a single monomer such as propylene, which are made herein, sometimes exhibit unusual properties compared to their "normal" homopolymers. For instance, such a homopolypropylene usually would have about 1000 methyl groups per 1000 methylene groups. Polypropylenes made herein typically have about half that many methyl groups, and in addition have some longer chain branches. Other α -olefins often give polymers whose microstructure is analogous to these polypropylenes when the above catalysts are used for the polymerization.

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These polypropylenes often exhibit exceptionally low glass transition temperatures (Tg's). "Normal" polypropylene has a Tg of about -17°C, but the polypropylenes herein have a Tg of -30°C or less, preferably about -35°C or less, and more preferably about -40°C or less. These Tg's are measured by Differential Scanning Calorimetry at a heating rate of 10°C/min, and the Tg is taken as the midpoint of the transition. These polypropylenes preferably have at least 50 branches (methyl groups) per 1000 carbon atoms, more preferably at least about 100 branches per 1000 methylene groups.

Previously, when cyclopentene was coordination polymerized to higher molecular weights, the resulting polymer was essentially intractable because of its very high melting point, greatly above 300°C. Using the catalysts here to homopolymerize cyclopentene results in a polymer that is tractable, i.e., may be reformed, as by melt forming. Such polymers have an end of melting point of about 320°C or less, preferably about 300°C or less, or a melting point of about 275°C or less, preferably about 250°C or less. The melting point is determined by Differential Scanning

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Calorimetry at a heating rate of 15°C/min, and taking the maximum of the melting endotherm as the melting point. However these polymers tend to have relatively diffuse melting points, so it is preferred to measure 5 the "melting point" by the end of melting point. method is the same, except the end of melting is taken as the end (high temperature end) of the melting endotherm which is taken as the point at which the DSC signal returns to the original (extrapolated) baseline. Such polymers have an average degree of polymerization (average number of cyclopentene repeat units per polymer chain) of about 10 or more, preferably about 30 or more, and more preferably about 50 or more.

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In these polymers, enchainment of the cyclopentene repeat units is usually as cis-1,3-pentylene units, in contrast to many prior art cyclopentenes which were enchained as 1,2-cyclopentylene units. It is preferred that about 90 mole percent or more, more preferably about 95 mole percent or more of the enchained cyclopentene units be enchained as 1,3-cyclopentylene units, which are preferably cis-1,3-cyclopentylene units.

The X-ray powder diffraction pattern of the instant poly(cyclopentenes) is also unique. To produce cyclopentene polymer samples of uniform thickness for X-ray measurements, powder samples were compressed into disks approximately 1 mm thick and 32 mm in diameter. X-ray powder diffraction patterns of the samples were collected over the range $10\text{--}50^{\circ}$ 2θ . The diffraction data were collected using an automated Philips $\theta \text{-}\theta$ diffractometer (Philips X'pert System) operating in the symmetrical transmission mode (Ni-filtered CuKa radiation, equipped with a diffracted beam collimator (Philips Thin Film Collimator system), Xe filled proportional detector, fixed step mode (0.05°/step), 12.5 sec./step, 1/4° divergence slit). Reflection positions were identified using the peak finding routine in the APD suite of programs provided with the

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X'pert System. The X-ray powder diffraction pattern had reflections at approximately 17.3° , 19.3° , 24.2° , and 40.7° 20, which correspond to d-spacings of approximately 0.512, 0.460, 0.368 and 0.222 nm, respectively. These polymers have a monoclinic unit cell of the approximate dimensions: a=0.561 nm; b=0.607 nm; c=7.37 nm; and g=123.2°.

Copolymers of cyclopentene and various other olefins may also be made. For instance a copolymer of ethylene and cyclopentene may also be made. In such a 10 copolymer it is preferred that at least 50 mole percent, more preferably at least about 70 mole percent, of the repeat units are derived from cyclopentene. As also noted above, many of the polymerization systems described herein produce 15 polyethylenes that have considerable branching in them. Likewise the ethylene units which are copolymerized with the cyclopentene herein may also be branched, so it is preferred that there be at least 20 branches per 1000 methylene carbon atoms in such copolymers. 20 this instance, the "methylene carbon atoms" referred to in the previous sentence do not include methylene groups in the cyclopentene rings. Rather it includes methylene groups only derived from ethylene or other olefin, but not cyclopentene. 25

Another copolymer that may be prepared is one from cyclopentene and an $\alpha\text{-olefin},$ more preferably a linear $\alpha\text{-olefin}.$ It is preferred in such copolymers that repeat units derived from cyclopentene are 50 mole percent or more of the repeat units. As mentioned above, $\alpha\text{-olefins}$ may be enchained in a 1, ω fashion, and it is preferred that at least 10 mole percent of the repeat units derived from the $\alpha\text{-olefin}$ be enchained in such a fashion. Ethylene may also be copolymerized with the cyclopentene and $\alpha\text{-olefin}.$

Poly(cyclopentene) and copolymers of cyclopentene, especially those that are (semi)crystalline, may be used as molding and extrusion resins. They may contain

various materials normally found in resins, such as fillers, reinforcing agents, antioxidants, antiozonants, pigments, tougheners, compatibilizers, dyes, flame retardant, and the like. These polymers may also be drawn or melt spun into fibers. Suitable tougheners and compatibilizers include polycyclopentene resin which has been grafted with maleic anhydride, an grafted EPDM rubber, a grafted EP rubber, a functionalized styrene/butadiene rubber, or other rubber which has been modified to selectively bond to components of the two phases.

In all of the above homo- and copolymers of cyclopentene, where appropriate, any of the preferred state may be combined any other preferred state(s).

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The homo- and copolymers of cyclopentene described above may used or made into certain forms as described below:

- nay be part of a polymer blend. That is they may be mixed in any proportion with one or more other polymers which may be thermoplastics and/or elastomers. Suitable polymers for blends are listed below in the listing for blends of other polymers described herein. One preferred type of polymer which may be blended is a toughening agent or compatibilizer, which is often elastomeric and/or contains functional groups which may help compatibilize the mixture, such as epoxy or carboxyl.
- 2. The polycyclopentenes described herein are useful in a nonwoven fabric comprising fibrillated three-dimensional network fibers prepared by using of a polycyclopentene resin as the principal component. It can be made by flash-spinning a homogeneous solution containing a polycyclopentene. The resultant nonwoven fabric is excellent in heat resistance, dimensional stability and solvent resistance.
 - 3. A shaped part of any of the cyclopentene containing resins. This part may be formed by

injection molding, extrusion, and thermoforming. Exemplary uses include molded part for automotive use, medical treatment container, microwave-range container, food package container such as hot packing container, oven container, retort container, etc., and heat-resisting transparent container such as heat-resisting bottle.

4. A sheet or film of any of the cyclopentene containing resins. This sheet or film may be clear and may be used for optical purposes (i.e. breakage resistant glazing). The sheet or film may be oriented or unoriented. Orientation may be carried out by any of the known methods such a uniaxial or biaxial drawing. The sheet or film may be stampable or thermoformable.

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- 5. The polycyclopentene resins are useful in nonwoven fabrics or microfibers which are produced by melt-blowing a material containing as a main component a polycyclopentene. A melt-blowing process for producing a fabric or fiber comprises supplying a polycyclopentene in a molten form from at least one orifice of a nozzle into a gas stream which attenuates the molten polymer into microfibers. The nonwoven fabrics are excellent in heat-resistant and chemical resistant characteristics, and are suitable for use as medical fabrics, industrial filters, battery separators and so forth. The microfibers are particularly useful in the field of high temperature filtration, coalescing and insulation.
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 6. A laminate in which one or more of the layers comprises a cyclopentene resin. The laminate may also contain adhesives, and other polymers in some or all of the layers, or other materials such as paper, metal foil, etc. Some or all of the layers, may be oriented in the same or different directions. The laminate as a whole may also be oriented. Such materials are useful for containers, or other uses where barrier properties are required.

7. A fiber of a cyclopentene polymer. This fiber may be undrawn or drawn to further orient it. It is useful for apparel and in industrial application where heat resistance and/or chemical resistance are important.

8. A foam or foamed object of a cyclopentene polymer. The foam may be formed in any conventional manner such as by using blowing agents.

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9. The cyclopentene resins may be microporous membranes. They may be used in process wherein semipermeable membranes are normally used.

In addition, the cyclopentene resins may be treated or mixed with other materials to improve certain properties, as follows:

- 1. They may further be irradiated with electron rays. This often improves heat resistance and/or chemical resistance, and is relatively inexpensive. Thus the molding is useful as a material required to have high heat resistance, such as a structural material, a food container material, a food wrapping material or an electric or electronic part material, particularly as an electric or electronic part material, because it is excellent in soldering resistance.
- 2. Parts with a crystallinity of at least 20% 25 may be obtained by subjecting cyclopentene polymers having an end of melting point between 240 and 300°C to heat treatment (annealing) at a temperature of 120°C to just below the melting point of the polymer. Preferred conditions are a temperature of 150 to 280°C. for a 30 period of time of 20 seconds to 90 minutes, preferably to give a cyclopentene polymer which has a heat deformation temperature of from 200 to 260°C. parts have good physical properties such as heat resistance and chemical resistance, and thus are useful 35 for, for example, general construction materials, electric or electronic devices, and car parts.

- 3. Cyclopentene resins may be nucleated to promote crystallization during processing. An example would be a polycyclopentene resin composition containing as main components (A) 100 parts by weight of a polycyclopentene and (B) 0.01 to 25 parts by weight of one or more nucleating agents selected from the group consisting of (1) metal salts of organic acids, (2) inorganic compounds, (3) organophosphorus compounds, and/or (4) metal salts of ionic hydrocarbon copolymer. Suitable nucleating agents may be sodium methylenebis(2,4-di-tertbutylphenyl) acid phosphate, sodium bis(4-tert-butylphenyl) phosphate, aluminum p-(tert-butyl) benzoate, talc, mica, or related species. These could be used in a process for producing polycyclopentene resin moldings by molding the above polycyclopentene resin composition at a temperature above their melting point.
- 4. Flame retardants and flame retardant combinations may be added to a cyclopentene polymer.

 Suitable flame retardants include a halogen-based or phosphorus-based flame retardant, antimony trioxide, antimony pentoxide, sodium antimonate, metallic antimony, antimony trichloride, antimony pentachloride, antimony trisulfide, antimony pentasulfide, zinc borate, barium metaborate or zirconium oxide. They may be used in conventional amounts.
 - 5. Antioxidants may be used in conventional amounts to improve the stability of the cyclopentene polymers. For instance 0.005 to 30 parts by weight, per 100 parts by weight of the cyclopentene polymer, of an antioxidant selected from the group consisting of a phosphorous containing antioxidant, a phenolic antioxidant or a combination thereof. The phosphorous containing antioxidant may be a monophosphite or diphosphite or mixture thereof and the phenolic antioxidant may be a dialkyl phenol, trialkyl phenol, diphenylmonoalkoxylphenol, a tetraalkyl phenol, or a mixture thereof. A sulfur-containing antioxidant may

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also be used alone or in combination with other antioxidants.

- 6. Various fillers or reinforcers, such as particulate or fibrous materials, may be added to improve various physical properties.
- obtained by the use of specific types of materials. Electrically conductive materials such as fine metallic wires or graphite may be used to render the polymer electrically conductive. The temperature coefficient of expansion may be regulated by the use of appropriate fillers, and it may be possible to even obtain materials with positive coefficients of expansion. Such materials are particularly useful in electrical and electronic parts.
- 8. The polymer may be crosslinked by irradiation or chemically as by using peroxides, optionally in the presence of suitable coagents. Suitable peroxides include benzoyl peroxide, lauroyl peroxide, dicumyl peroxide, tert-butyl peroxide, tert-butylperoxybenzoate, tert-butylcumyl peroxide, tert-butylhydroperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,1-labis(tert-
- 25 butylperoxyisopropyl)benzene, 1,1-bis(tertbutylperoxy)-3,3,5- trimethylcyclohexane, n-butyl-4,4bis(tert-butylperoxy)valerate, 2,2-bis(tertbutylperoxy)butane and tert-butylperoxybenzene.

When polymerizing cyclopentene, it has been found that some of the impurities that may be found in cyclopentene poison or otherwise interfere with the polymerizations described herein. Compounds such as 1,3-pentadiene (which can be removed by passage through 5A molecular sieves), cyclopentadiene (which can be removed by distillation from Na), and methylenecyclobutane (which can be removed by

distillation from polyphosphoric acid), may interfere

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with the polymerization, and their level should be kept as low as practically possible.

The above polymers (in general) are useful in many applications. Crystalline high molecular weight polymers are useful as molding resins, and for films for use in packaging. Amorphous resins are useful as elastomers, and may be crosslinked by known methods, such as by using free radicals. When such amorphous resins contain repeat units derived from polar monomers they are oil resistant. Lower molecular weight polymers are useful as oils, such as in polymer processing aids. When they contain polar groups, particularly carboxyl groups, they are useful in adhesives.

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In many of the above polymerizations, the transition metal compounds employed as (part of the) catalysts contain(s) (a) metal atom(s) in a positive oxidation state. In addition, these complexes may have a square planar configuration about the metal, and the metal, particularly nickel or palladium, may have a d8 20 electronic configuration. Thus some of these catalysts may be said to have a metal atom which is cationic and has a d8-square planar configuration.

In addition these catalysts may have a bidentate ligand wherein coordination to the transition metal is 25 through two different nitrogen atoms or through a nitrogen atom and a phosphorus atom, these nitrogen and phosphorus atoms being part of the bidentate ligand. It is believed that some of these compounds herein are effective polymerization catalysts at least partly 30 because the bidentate ligands have sufficient steric bulk on both sides of the coordination plane (of the square planar complex). Some of the Examples herein with the various catalysts of this type illustrate the degree of steric bulk which may be needed for such 35 catalysts. If such a complex contains a bidentate ligand which has the appropriate steric bulk, it is

believed that it produces polyethylene with a degree of polymerization of at least about 10 or more.

It is also believed that the polymerization catalysts herein are effective because unpolymerized 5 olefinic monomer can only slowly displace from the complex a coordinated olefin which may be formed by $\beta\text{-}$ hydride elimination from the growing polymer chain which is attached to the transition metal. The displacement can occur by associative exchange. Increasing the steric bulk of the ligand slows the rate 10 of associative exchange and allows polymer chain growth. A quantitative measure of the steric bulk of the bidentate ligand can be obtained by measuring at -85°C the rate of exchange of free ethylene with complexed ethylene in a complex of formula (XI) as 15 shown in equation 1 using standard 1H NMR techniques, which is called herein the Ethylene Exchange Rate (EER). The neutral bidentate ligand is represented by YN where Y is either N or P. The EER is measured in this system. In this measurement system the metal is 20 always Pd, the results being applicable to other metals as noted below. Herein it is preferred for catalysts to contain bidentate ligands for which the second order rate constant for Ethylene Exchange Rate is about $20,000 \text{ L-mol}^{-1}\text{s}^{-1}$ or less when the metal used in the 25 polymerization catalyst is palladium, more preferably about 10,000 L-mol⁻¹s⁻¹ or less, and more preferably about 5,000 L-mol⁻¹s⁻¹ or less. When the metal in the polymerization catalyst is nickel, the second order rate constant (for the ligand in EER measurement) is 30 about 50,000 L-mol⁻¹s⁻¹, more preferably about 25,000 Lmol⁻¹s⁻¹ or less, and especially preferably about 10,000 L-mol⁻¹s⁻¹ or less. Herein the EER is measured using the compound (XI) in a procedure (including temperature) described in Examples 21-23.

In these polymerizations it is preferred if the bidentate ligand is an α -diimine. It is also preferred if the olefin has the formula $R^{17}CH=CH_2$, wherein R^{17} is hydrogen or n-alkyl.

In general for the polymers described herein, blends may be prepared with other polymers, and such other polymers may be elastomers, thermoplastics or thermosets. By elastomers are generally meant polymers whose Tg (glass transition temperature) and Tm (melting point), if present, are below ambient temperature, usually considered to be about 20°C. Thermoplastics are those polymers whose Tg and/or Tm are at or above ambient temperature. Blends can be made by any of the common techniques known to the artisan, such as solution blending, or melt blending in a suitable apparatus such as a single or twin-screw extruder. Specific uses for the polymers of this application in the blends or as blends are listed below.

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Blends may be made with almost any kind of elastomer, such as EP, EPDM, SBR, natural rubber, polyisoprene, polybutadiene, neoprene, butyl rubber, styrene-butadiene block copolymers, segmented polyester-polyether copolymers, elastomeric polyurethanes, chlorinated or chlorosulfonated polyethylene, (per) fluorinated elastomers such as copolymers of vinylidene fluoride, hexafluoropropylene and optionally tetrafluoroethylene, copolymers of tetrafluoroethylene, copolymers of tetrafluoroethylene and propylene.

Suitable thermoplastics which are useful for blending with the polymers described herein include: polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), and poly(ethylene

adipate); polyamides such as nylon-6, nylon-6,6, nylon-12, nylon-12,12, nylon-11, and a copolymer of hexamethylene diamine, adipic acid and terephthalic acid; fluorinated polymers such as copolymers of ethylene and vinylidene fluoride, copolymers of 5 tetrafluoroethylene and hexafluoropropylene, copolymers of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) such as perfluoro(propyl vinyl ether), and poly(vinyl fluoride); other halogenated polymers such a poly(vinyl chloride) and poly(vinylidene chloride) and 10 its copolymers; polyolefins such as polyethylene, polypropylene and polystyrene, and copolymers thereof; (meth)acrylic polymers such a poly(methyl methacrylate) and copolymers thereof; copolymers of olefins such as ethylene with various (meth) acrylic monomers such as 15 alkyl acrylates, (meth)acrylic acid and ionomers thereof, and glycidyl (meth)acrylate); aromatic polyesters such as the copolymer of Bisphenol A and terephthalic and/or isophthalic acid; and liquid 20 crystalline polymers such as aromatic polyesters or aromatic poly(ester-amides).

Suitable thermosets for blending with the polymers described herein include epoxy resins, phenolformaldehyde resins, melamine resins, and unsaturated polyester resins (sometimes called thermoset polyesters). Blending with thermoset polymers will often be done before the thermoset is crosslinked, using standard techniques.

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The polymers described herein may also be blended with uncrosslinked polymers which are not usually considered thermoplastics for various reasons, for instance their viscosity is too high and/or their melting point is so high the polymer decomposes below the melting temperature. Such polymers include poly(tetrafluoroethylene), aramids such as poly(p-phenylene terephthalate) and poly(m-phenylene isophthalate), liquid crystalline polymer such as

poly(benzoxazoles), and non-melt processible polyimides which are often aromatic polyimides.

All of the polymers disclosed herein may be mixed with various additives normally added to elastomers and thermoplastics [see EPSE (below), vol. 14, p. 327-410]. For instance reinforcing, non-reinforcing and conductive fillers, such as carbon black, glass fiber, minerals such as clay, mica and talc, glass spheres, barium sulfate, zinc oxide, carbon fiber, and aramid fiber or fibrids, may be used. Antioxidants, antiozonants, pigments, dyes, delusterants, compounds to promote crosslinking may be added. Plasticizers such as various hydrocarbon oils may also be used.

The following listing is of some uses for polyolefins, which are made from linear olefins and do not include polar monomers such as acrylates, which are disclosed herein. In some cases a reference is given which discusses such uses for polymers in general. All of these references are hereby included by reference. For the references, "U" refers to W. Gerhartz, et al., 20 Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed. VCH Verlagsgesellschaft mBH, Weinheim, for which the volume and page number are given, "ECT3" refers to the H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, "ECT4" refers to the J. I Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPST" refers to H. F. Mark, et al., Ed., Encyclopedia 30 of Polymer Science and Technology, 1st Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPSE" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley & Sons, New York, for which volume and 35 page numbers are given, and "PM" refers to J. A. Brydson, ed., Plastics Materials, 5 Ed., Butterworth-Heinemann, Oxford, UK, 1989, and the page is given. In

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these uses, a polyethylene, polypropylene and a copolymer of ethylene and propylene are preferred.

- 1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers. Elastomeric and/or relatively low molecular weight polymers are preferred.
- 2. An oil additive for smoke suppression in single-stroke gasoline engines is another use. Elastomeric polymers are preferred.
- 3. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a carpet installation adhesive.
- 4. Lubricating oil additives as Viscosity Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene copolymer with acrylates or other polar monomers will also function as Viscosity Index Improvers for multigrade engine oil with the additional advantage of providing some dispersancy. 5. Polymer for coatings and/or penetrants for the protection of various porous items such as lumber and masonry, particularly out-of-doors. The polymer may be in a suspension or emulsion, or may be dissolved in a solvent.
 - 6. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower molecular weight polymers are often used.
 - 7. The polymers may be grafted with various compounds particularly those that result in functional groups such as epoxy, carboxylic anhydride (for instance as with a free radically polymerized reaction with maleic anhydride) or carboxylic acid (EPSE, vol. 12, p. 445). Such functionalized polymers are particularly useful as tougheners for various thermoplastics and thermosets when blended. When the

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polymers are elastomers, the functional groups which are grafted onto them may be used as curesites to crosslink the polymers. Maleic anhydride-grafted randomly-branched polyolefins are useful as tougheners for a wide range of materials (nylon, PPO, PPO/styrene alloys, PET, PBT, POM, etc.); as tie layers in multilayer constructs such as packaging barrier films; as hot melt, moisture-curable, and coextrudable adhesives; or as polymeric plasticizers. andhydride-grafted materials may be post reacted with, 10 for example; amines, to form other functional materials. Reaction with aminopropyl trimethoxysilane would allow for moisture-curable materials. Reactions with di- and tri-amines would allow for viscosity 15 modifications.

- 8. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving.
- 9. The polymers may be used as base resins for chlorination or chlorosulfonation for making the corresponding chlorinated or chlorosulfonated elastomers. The unchlorinated polymers need not be elastomers themselves.
 - 10. Wire insulation and jacketing may be made from any of the polyolefins (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.
- 30 11. The polymers, particularly the elastomers, may be used as tougheners for other polyolefins such as polypropylene and polyethylene.
 - 12. The base for synthetic lubricants (motor oils) may be the highly branched polyolefins described herein (ECT3, vol. 14, p. 496-501).
 - 13. The branched polyolefins herein can be used as drip suppressants when added to other polymers.

- 14. The branched polyolefins herein are especially useful in blown film applications because of their particular rheological properties (EPSE, vol. 7, p. 88-106). It is preferred that these polymers have some crystallinity.
- 15. The polymer described herein can be used to blend with wax for candles, where they would provide smoke suppression and/or drip control.
- 16. The polymers, especially the branched polymers, are useful as base resins for carpet backing, especially for automobile carpeting.
 - 17. The polymers, especially those which are relatively flexible, are useful as capliner resins for carbonated and noncarbonated beverages.
- 18. The polymers, especially those having a relatively low melting point, are useful as thermal transfer imaging resins (for instance for imaging teeshirts or signs).
- 19. The polymers may be used for extrusion or 20 coextrusion coatings onto plastics, metals, textiles or paper webs.
 - 20. The polymers may be used as a laminating adhesive for glass.
- 21. The polymers are useful as for blown or
 25 cast films or as sheet (see EPSE, vol. 7 p. 88-106;
 ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff).
 The films may be single layer or multilayer, the
 multilayer films may include other polymers, adhesives,
 etc. For packaging the films may be stretch-wrap,
- 30 shrink-wrap or cling wrap. The films are useful form many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.
- 22. The polymers may be used to form flexible or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some

crystallinity. The polymer of the foams may be crosslinked.

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- 23. In powdered form the polymers may be used to coat objects by using plasma, flame spray or fluidized bed techniques.
- 24. Extruded films may be formed from these polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.
- 10 25. The polymers, especially those that are elastomeric, may be used in various types of hoses, such as automotive heater hose.
 - 26. The polymers, especially those that are branched, are useful as pour point depressants for fuels and oils.
- 27. These polymers may be flash spun to nonwoven fabrics, particularly if they are crystalline (see EPSE vol. 10, p. 202-253) They may also be used to form spunbonded polyolefins (EPSE, vol. 6, p. 756-20 760). These fabrics are suitable as house wrap and geotextiles.
- 28. The highly branched, low viscosity polyolefins would be good as base resins for masterbatching of pigments, fillers, flame-retardants, and related additives for polyolefins. 29. The polymers 25 may be grafted with a compound containing ethylenic unsaturation and a functional group such as a carboxyl group or a derivative of a carboxyl group, such as ester, carboxylic anhydride of carboxylate salt. A minimum grafting level of about 0.01 weight percent of 30 grafting agent based on the weight of the grafted polymer is preferred. The grafted polymers are useful as compatibilizers and/or tougheners. Suitable grafting agents include maleic, acrylic, methacrylic, itaconic, crotonic, alpha-methyl crotonic and cinnamic acids, anhydrides, esters and their metal salts and fumaric acid and their esters, anhydrides (when

appropriate) and metal salts.

Copolymers of linear olefins with 4vinylcyclohexene and other dienes may generally be used for all of the applications for which the linear olefins polymers(listed above) may be used. addition they may be sulfur cured, so they generally can be used for any use for which EPDM polymers are used, assuming the olefin/4-vinylcyclohexene polymer is elastomeric.

Also described herein are novel copolymers of 10 linear olefins with various polar monomers such as acrylic acid and acrylic esters. Uses for these polymers are given below. Abbreviations for references describing these uses in general with polymers are the same as listed above for polymers made from linear olefins.

- 1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers. Elastomeric and/or relatively low molecular weight polymers are preferred.
- 2. The polymers are useful as base resins for 20 hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a carpet installation adhesive. 25
 - 3. Base polymer for caulking of various kinds is another use. An elastomer is preferred. molecular weight polymers are often used.
- 4. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical 30 properties of the asphalt and/or extend the life of asphalt paving, see U.S. patent 3,980,598.
- 5. Wire insulation and jacketing may be made from any of the polymers (see EPSE, vol. 17, p. 828-In the case of elastomers it may be preferable 35 to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

6. The polymers, especially the branched polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

- 7. The polymers may be used for extrusion or coextrusion coatings onto plastics, metals, textiles or paper webs.
 - 8. The polymers may be used as a laminating adhesive for glass.

- 9. The polymers are useful as for blown or cast films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For packaging the films may be stretch-wrap, shrink-wrap or cling wrap. The films are useful form many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.
- or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the polymers have some crystallinity. The polymer of the foams may be crosslinked.
 - 11. In powdered form the polymers may be used to coat objects by using plasma, flame spray or fluidized bed techniques.
- 12. Extruded films may be formed from these
 30 polymers, and these films may be treated, for example
 drawn. Such extruded films are useful for packaging of
 various sorts.
 - 13. The polymers, especially those that are elastomeric, may be used in various types of hoses, such as automotive heater hose.
 - 14. The polymers may be used as reactive diluents in automotive finishes, and for this purpose

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it is preferred that they have a relatively low molecular weight and/or have some crystallinity.

- 15. The polymers can be converted to ionomers, which when the possess crystallinity can be used as molding resins. Exemplary uses for these ionomeric molding resins are golf ball covers, perfume caps, sporting goods, film packaging applications, as tougheners in other polymers, and usually extruded) detonator cords.
- 16. The functional groups on the polymers can be used to initiate the polymerization of other types of monomers or to copolymerize with other types of monomers. If the polymers are elastomeric, they can act as toughening agents.
- 15 17. The polymers can act as compatibilizing agents between various other polymers.
 - 18. The polymers can act as tougheners for various other polymers, such as thermoplastics and thermosets, particularly if the olefin/polar monomer polymers are elastomeric.
 - 19. The polymers may act as internal plasticizers for other polymers in blends. A polymer which may be plasticized is poly(vinyl chloride).
- 20. The polymers can serve as adhesives between 25 other polymers.
 - 21. With the appropriate functional groups, the polymers may serve as curing agents for other polymers with complimentary functional groups (i.e., the functional groups of the two polymers react with each other).
 - 22. The polymers, especially those that are branched, are useful as pour point depressants for fuels and oils.
- 23. Lubricating oil additives as Viscosity

 Index Improvers for multigrade engine oil (ECT3, Vol
 14, p. 495-496) are another use. Branched polymers are
 preferred. Ethylene copolymer with acrylates or other
 polar monomers will also function as Viscosity Index

Improvers for multigrade engine oil with the additional advantage of providing some dispersancy.

- 24. The polymers may be used for roofing membranes.
 - 25. The polymers may be used as additives to various molding resins such as the so-called thermoplastic olefins to improve paint adhesion, as in automotive uses.
- 10 Polymers with or without polar monomers present are useful in the following uses. Preferred polymers with or without polar monomers are those listed above in the uses for each "type".
- 1. A flexible pouch made from a single layer or multilayer film (as described above) which may be used for packaging various liquid products such as milk, or powder such as hot chocolate mix. The pouch may be heat sealed. It may also have a barrier layer, such as a metal foil layer.
- 2. A wrap packaging film having differential cling is provided by a film laminate, comprising at least two layers; an outer reverse which is a polymer (or a blend thereof) described herein, which contains a tackifier in sufficent amount to impart cling properties; and an outer obverse which has a density of at least about 0.916 g/mL which has little or no cling, provided that a density of the outer reverse layer is at least 0.008 g/mL less than that of the density of
- the outer obverse layer. It is preferred that the outer obverse layer is linear low density polyethylene, and the polymer of the outer obverse layer have a density of less than 0.90 g/mL. All densities are measured at 25°C.
- 3. Fine denier fibers and/or multifilaments.

 These may be melt spun. They may be in the form of a filament bundle, a non-woven web, a woven fabric, a knitted fabric or staple fiber.

- 4. A composition comprising a mixture of the polymers herein and an antifogging agent. This composition is especially useful in film or sheet form because of its antifogging properties.
- 5. Elastic, randomly-branched olefin polymers are 5 disclosed which have very good processability, including processing indices (PI's) less than or equal to 70 percent of those of a comparative linear olefin polymer and a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the 10 critical shear rate at the onset of surface melt fracture of a traditional linear olefin polymer at about the same I2 and Mw/Mn. The novel polymers may have higher low/zero shear viscosity and lower high shear viscosity than comparative linear olefin polymers 15 made by other means. These polymers may be characterized as having: a) a melt flow ratio, I10/I2, ≥ 5.63, b) a molecular weight distribution, Mw/Mn, defined by the equation: $Mw/Mn \le (I10/I2)-4.63$, and c) a critical shear rate at onset of surface melt fracture 20 of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn. Some blends of these polymer are characterized as having: a) a melt flow ratio, I10/I2, ≥ 5.63, b) a 25 molecular weight distribution, Mw/Mn, defined by the equation: $Mw/Mn \le (I10/I2)-4.63$, and c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear - 30 olefin polymer having about the same I2 and Mw/Mn and (b) at least one other natural or synthetic polymer chosen from the polymer of claims 1, 3, 4, 6, 332, or 343, a conventional high density polyethylene, low density polyethylene or linear low density polyethylene 35 polymer. The polymers may be further characterized as having a melt flow ratio, I10/I2, ≥ 5.63, a molecular weight distribution, Mw/Mn, defined by the equation:

Mw/Mn ≤ (I10/I2)-4.63, and a critical shear stress at onset of gross melt fracture of greater than about 400 kPa (4x10⁶ dyne/cm²) and their method of manufacture are disclosed. The randomly-branched olefin polymers preferably have a molecular weight distribution from about 1.5 to about 2.5. The polymers described herein often have improved processability over conventional olefin polymers and are useful in producing fabricated articles such as fibers, films, and molded parts. For this paragraph, the value I2 is measured in accordance with ASTM D-1238-190/2.16 and I10 is measured in accordance with ASTM D-1238-190/10; critical shear rate at onset of surface melt fracture and processing index (PI) are defined in U.S. Patent 5,278,272, which is hereby included by reference.

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In another process described herein, the product of the process described herein is an α -olefin. It is preferred that in the process a linear α -olefin is produced. It is also preferred that the α -olefin contain 4 to 32, preferably 8 to 20, carbon atoms.

(XXXI)

When (XXXI) is used as a catalyst, a neutral Lewis acid or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion is also present as part of the catalyst system (sometimes called a "first compound" in the claims). By a "neutral Lewis acid" is meant a compound which is a Lewis acid capable for abstracting X from (I) to form a weakly coordinating anion. The neutral Lewis acid is originally uncharged (i.e., not ionic). Suitable neutral Lewis acids include SbF₅, Ar₁B (wherein Ar is

aryl), and BF_3 . By a cationic Lewis acid is meant a cation with a positive charge such as Ag^+ , H^+ , and Na^+ .

A preferred neutral Lewis acid is an alkyl aluminum compound, such as R^9_3Al , R^9_2AlCl , R^9AlCl_2 , and " R^9AlO " (alkylaluminoxane), wherein R^9 is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Suitable alkyl aluminum compounds include methylaluminoxane, $(C_2H_5)_2AlCl$, $C_2H_5AlCl_2$, and $[(CH_3)_2CHCH_2]_3Al$.

Relatively noncoordinating anions are known in the art, and the coordinating ability of such anions is known and has been discussed in the literature, see for instance W. Beck., et al., Chem. Rev., vol. 88 p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. Among such anions are those formed from the aluminum compounds in the immediately preceding paragraph and X, including R, AlX, R, AlCl2X,

include BAF {BAF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF₆, PF₆, and BF₄, trifluoromethanesulfonate, p-toluenesulfonate, $(R_fSO_2)_2N$, and $(C_6F_5)_4B$.

and "R'AlOX". Other useful noncoordinating anions

The temperature at which the process is carried out is about -100°C to about $+200^{\circ}\text{C}$, preferably about 0°C to about 150°C , more preferably about 25°C to about 100°C . It is believed that at higher temperatures, lower molecular weight α -olefins are produced, all other factors being equal. The pressure at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range. It is also believed that increasing the pressure increases the relative amount of α -olefin (as opposed to internal olefin) produced.

The process to make α -olefins may be run in a solvent (liquid), and that is preferred. The solvent may in fact be the α -olefin produced. Such a process may be started by using a deliberately added solvent

which is gradually displaced as the reaction proceeds. By solvent it is not necessarily meant that any or all of the starting materials and/or products are soluble in the (liquid) solvent.

In (I) it is preferred that R^3 and R^4 are both hydrogen or methyl or R^3 and R^4 taken together are

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10 It is also preferred that each of Q and S is independently chlorine or bromine, and it is more preferred that both of Q and S in (XXXI) are chlorine or bromine.

In (XXXI) R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl. What these groups are greatly determines whether the α -olefins of this process are made, or whether higher polymeric materials, i.e., materials containing over 25 ethylene units, are coproduced or produced almost exclusively. If R^2 and R^5 are highly sterically hindered about the nickel atom, the tendency is to produce higher polymeric material. For instance, when R^2 and R^5 are both 2,6-diisopropylphenyl mostly higher polymeric material is produced. However, when R^2 and R^5 are both phenyl, mostly the α -olefins of this process are produced. Of course this will also be influenced by other reaction conditions such as temperature and pressure, as noted above. Useful groups for R^2 and R^5 are phenyl, and p-methylphenyl.

As is understood by the artisan, in cligomerization reactions of ethylene to produce α -olefins, usually a mixture of such α -olefins is obtained containing a series of such α -olefins differing from one another by two carbon atoms (an ethylene unit). The process for preparing α -olefins described herein produces products with a high

percentage of terminal olefinic groups (as opposed to internal olefinic groups). The product mixture also contains a relatively high percentage of molecules which are linear. Finally relatively high catalyst efficiencies can be obtained.

The $\alpha\text{-olefins}$ described as being made herein may also be made by contacting ethylene with one of the compounds

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(III)

or

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wherein R^2 , R^3 , R^4 , and R^5 are as defined (and preferred) as described above (for the preparation of α -olefins), and T^1 is hydrogen or n-alkyl containing up to 38 carbon atoms, Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, U is n-alkyl containing up to 38 carbon atoms, and X is a noncoordinating anion (see above). The process conditions for making α -olefins using (III) or (XXXIV) are the same as for using (XXXI) to make these compounds except a Lewis or Bronsted acid need not be present. Note that the double line in (XXXIV) represents a coordinated

ethylene molecule. (XXXIV) may be made Trom (II) by reaction of (III) with ethylene. In other words, (XXXIV) may be considered an active intermediate in the formation of α -olefin from (III). Suitable groups for Z include dialkyl ethers such as diethyl ether, and alkyl nitriles such as acetonitrile.

In general, α -olefins can be made by this process using as a catalyst a Ni[II] complex of an α -dimine of formula (VIII), wherein the Ni[II] complex is made by any of the methods which are described above, using Ni[0], Ni[I] or Ni[II] precursors. All of the process conditions, and preferred groups on (VIII), are the same as described above in the process for making α -olefins.

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EXAMPLES

In the Examples, the following convention is used for naming α -diimine complexes of metals, and the α diimine itself. The α -diimine is indicated by the letters "DAB". To the left of the "DAB" are the two 20 groups attached to the nitrogen atoms, herein usually called R² and R⁵. To the right of the "DAB" are the groups on the two carbon atoms of the α -diimine group, herein usually termed R³ and R⁴. To the right of all 25 this appears the metal, ligands attached to the metal (such as Q, S and T), and finally any anions (X), which when "free" anions are designated by a superscript minus sign (i.e., X). Of course if there is a "free". anion present, the metal containing moiety is cationic. Abbreviations for these groups are as described in the 30 Specification in the Note after Table 1. Analogous abbreviations are used for α -diimines, etc.

In the Examples, the following abbreviations are used:

ΔH: - heat of fusion

acac - acetylacetonate

Bu - butyl

t-BuA - t-butyl acrylate

DMA - Dynamic Mechanical Analysis DME - 1,2-dimethoxyethane DSC - Differential Scanning Calorimetry E - ethylene 5 EOC - end of chain Et - ethyl FC-75 - perfluoro(n-butyltetrahydrofuran) FOA - fluorinated octyl acrylate GPC - gel permeation chromatography 10 MA - methyl acrylate MAO - methylaluminoxane Me - methyl MeOH - methanol MMAO - a modified methylaluminoxane in which 15 about 25 mole percent of the methyl groups have been replaced by isobutyl groups M-MAO - see MMAO MMAO-3A - see MMAO Mn - number average molecular weight 20 MVK - methyl vinyl ketone Mw- weight average molecular weight Mz - viscosity average molecular weight PD or P/D - polydispersity, Mw/Mn Ph - phenyl 25 PMAO - see MAO PMMA - poly(methyl methacrylate) Pr - propyl PTFE - polytetrafluoroethylene RI - refractive index 30 RT (or rt) - room temperature TCE - 1,1,2,2-tetrachloroethane Tc - temperature of crystallization Td - temperature of decomposition Tq - qlass transition temperature 35 TGA - Thermogravimetric Analysis THF - tetrahydrofuran Tm - melting temperature

TO - turnovers, the number of moles of monomer polymerized per g-atom of metal in the catalyst used

UV - ultraviolet

Unless otherwise noted, all pressures are gauge 5 pressures.

In the Examples, the following procedure was used to quantitatively determine branching, and the distribution of branch sizes in the polymers (but not necessarily the simple number of branches as measured 10 by total number of methyl groups per 1000 methylene 100 MHz ¹³C NMR spectra were obtained on a Varian Unity 400 MHz spectrometer using a 10 mm probe on typically 15-20 wt% solutions of the polymers and 0.05 M Cr(acetylacetonate)₃ in 1,2,4-trichlorobenzene (TCB) unlocked at 120-140°C using a 90 degree pulse of 15 12.5 to 18.5 μ sec, a spectral width of 26 to 35 kHz, a relaxation delay of 5-9 s, an acquisition time of 0.64 sec and gated decoupling. Samples were preheated for at least 15 min before acquiring data. Data 20 acquisition time was typically 12 hr. per sample. $\mathtt{T}^{\mathtt{l}}$ values of the carbons were measured under these conditions to be all less than 0.9 s. The longest T^1 measured was for the Bu+, end of chain resonance at 14 ppm, which was 0.84 s. Occasionally about 16 vol. % 25 benzene-d, was added to the TCB and the sample was run Some samples were run in chloroform-d1, CDCl3dl, (locked) at 30°C under similar acquisition parameters. Tl's were also measured in CDCl3 at ambient temperature on a typical sample with 0.05 M 30 Cr(acetylacetonate) 3 to be all less than 0.68 s. In rare cases when Cr(acetylacetonate) 3 was not used, a 30-40 s recycle delay was used to insure quantitation. The glycidyl acrylate copolymer was run at 100°C with Cr(acetylacetonate)3. Spectra are referenced to the solvent - either the TCB highfield resonance at 127.8 35 ppm or the chloroform-d1 triplet at 77 ppm. spectrum was done on most samples to distinguish methyls and methines from methylenes. Methyls were

listinguished from methines by chemical shift. EOC is end-of-chain. Assignments reference to following naming scheme:

- 1. xBy: By is a branch of length y carbons; x is the carbon being discussed, the methyl at the end of the branch is numbered 1. Thus the second carbon from the end of a butyl branch is 2B4. Branches of length y or greater are designated as y⁺.
- xEBy: EB is an ester ended branch containing y 10 methylenes. x is the carbon being discussed, the first methylene adjacent to the ester carbonyl is labeled 1. Thus the second methylene from the end of a 5 methylene ester terminated branch would be 2EB5. 13C NMR of model compounds for EBy type branches for y=0 and y=5+ confirm the peak positions and assignments of these 15 In addition, a model compound for an EB1 branches. branch is consistent with 2 dimensional NMR data using the well know 2D NMR techniques of hsqc, hmbc, and hsqc-tocsy; the 2D data confirms the presence of the 20 EB5+, EB0, EB1 and other intermediate length EB branches
 - 3. The methylenes in the backbone are denoted with Greek letters which determine how far from a branch point methine each methylene is. Thus $\beta\beta$ (beta beta) B denotes the central methylene in the following PCHRCH₂CH₂CH₂CHRP. Methylenes that are three or more carbons from a branch point are designated as γ^+ (gamma+).
- 4. When x in xBy or xEBy is replaced by a M, the 30 methine carbon of that branch is denoted.

Integrals of unique carbons in each branch were measured and were reported as number of branches per 1000 methylenes (including methylenes in the backbone and branches). These integrals are accurate to +/- 5% relative for abundant branches and +/- 10 or 20% relative for branches present at less than 10 per 1000 methylenes.

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Such types of analyses are generally known, see for instance "A Quantitative Analysis of Low Density (Branched) Polyethylenes by Carbon-13 Fourier Transform Nuclear Magnetic Resonance at 67.9 MHz", D. E. Axelson, et al., Macromolecules 12 (1979) pp. 41-52; "Fine Branching Structure in High-Pressure, Low Density Polyethylenes by 50.10-MHz 13C NMR Analysis", T. Usami et al., Macromolecules 17 (1984) pp. 1757-1761; and "Quantification of Branching in Polyethylene by 13C NMR Using Paramagnetic Relaxation Agents", J. V. Prasad, et al., Eur. Polym. J. 27 (1991) pp. 251-254 (Note that this latter paper is believed to have some significant typographical errors in it).

It is believed that in many of the polymers

described herein which have unusual branching, i.e.,
they have more or fewer branches than would be expected
for "normal" coordination polymerizations, or the
distribution of sizes of the branches is different from
that expected, that "branches on branches" are also

present. By this is meant that a branch from the main
chain on the polymer may itself contain one or more
branches. It is also noted that the concept of a "main
chain" may be a somewhat semantic argument if there are
sufficient branches on branches in any particular

polymer.

By a polymer hydrocarbyl branch is meant a methyl group to a methine or quaternary carbon atom or a group of consecutive methylenes terminated at one end by a methyl group and connected at the other end to a methine or quaternary carbon atom. The length of the branch is defined as the number of carbons from and including the methyl group to the nearest methine or quaternary carbon atom, but not including the methine or quaternary carbon atom. If the number of consecutive methylene groups is "n" then the branch contains (or the branch length is) n+1. Thus the structure (which represents part of a polymer) -

For ester ended branches a similar definition is used. An ester branch refers to a group of consecutive methylene groups terminated at one end by an ester - COOR group, and connected at the other end to a methine or quaternary carbon atom. The length of the branch is defined as the number of consecutive methylene groups from the ester group to the nearest methine or quaternary carbon atom, but not including the methine or quaternary carbon atom. If the number of methylene groups is "n", then the length of the branch is n. Thus -CH2CH2CH(CH2CH2CH2CH(CH3)CH2COOR)CH2CH2CH2CH2-contains 2 branches, a methyl and an n=1 ester branch.

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The ¹³C NMR peaks for copolymers of cyclopentene and ethylene are described based on the labeling scheme and assignments of A. Jerschow et al, Macromolecules 1995, 28, 7095-7099. The triads and pentads are described as 1-cme, 1,3-ccmcc, 1,3-cmc, 2-cme, 2-cmc, 1,3-eme,3-cme, and 4,5-cmc, where e = ethylene, c = cyclopentene, and m = meta cyclopentene (i.e. 1,3 enchainment). The same labeling is used for cyclopentene/1-pentene copolymer substituting p = pentene for e. The synthesis of diimines is reported in the literature (Tom Dieck, H.; Svoboda, M.; Grieser, T. Z. Naturforsch 1981, 36b, 823-832. Kliegman, J. M.;

Example 1

[(2,6-i-PrPh),DABMe,]PdMeCl

30 Et₂O (75 mL) was added to a Schlenk flask containing CODPdMeCl (COD = 1,5-cyclooctadiene) (3.53 g, 13.3 mmol) and a slight excess of (2,6-i-PrPh)₂DABMe₂ (5.43 g, 13.4 mmol, 1.01 equiv). An orange precipitate began to form immediately upon 35 mixing. The reaction mixture was stirred overnight and the Et₂O and free COD were then removed via filtration. The product was washed with an additional 25 mL of Et₂O and then dried overnight in vacuo. A pale orange

Barnes, R. K. J. Org. Chem. 1970, 35, 3140-3143.)

Example 2

[(2,6-i-PrPh)2DABH2]PdMeCl

Following the procedure of Example 1, an orange powder was isolated in 97.1% yield: ^{1}H NMR (CD₂Cl₂, 400 MHz) δ 8.31 and 8.15 (s, 1 each, N=C(H)-C'(H)=N), $7.3 - 7.1 \text{ (m, 6, } H_{aryl}), 3.22 \text{ (septet, 2, } J = 6.80, }$ $CHMe_2$), 3.21 (septet, 2, J = 6.86, $C'HMe_2$), 1.362, 1.356, 1.183 and 1.178 (d, 6 each, J = 7.75 - 6.90; CHMeMe', C'HMeMe'), 0.67 (s, 3, PdMe); 13C NMR $(CD_2Cl_2, 100 \text{ MHz}) \delta 164.5 (J_{CH} = 179.0, N=C(H)), 160.6$ 10 $(J_{CH} = 178.0, N=C'(H)), 144.8 \text{ and } 143.8 \text{ (Ar, Ar':}$ C_{ipso}), 140.0 and 139.2 (Ar, Ar': C_o), 128.6 and 127.7 $(Ar, Ar': C_p)$, 124.0 and 123.4 $(Ar, Ar': C_m)$, 29.1 $(CHMe_2)$, 28.6 $(C'HMe_2)$, 24.7, 24.1, 23.1 and 22.7 (CHMeMe', C'HMeMe'), $3.0 (J_{CH} = 134.0, PdMe)$. Anal. 15 Calcd for $(C_{27}H_{39}ClN_2Pd)$: C, 60.79; H, 7.37; N, 5.25. Found: C, 60.63; H, 7.24; N, 5.25.

Example 3

[(2,6-MePh)₂DABMe₂]PdMeCl

Following the procedure of Example 1, a yellow powder was isolated in 90.6% yield: 1 H NMR (CD₂Cl₂, 400 MHz) δ 7.3 - 6.9 (m, 6, H_{aryl}), 2.22 (s, 6, Ar, Ar': Me), 2.00 and 1.97 (N=C(Me)-C'(Me)=N), 0.25 (s, 3, PdMe).

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Example 4

[(2,6-MePh)₂DABMe₂]PdMeCl

Following the procedure of Example 1, an orange powder was isolated in 99.0% yield: 1 H NMR (CD₂Cl₂, 400 MHz, 41 °C) δ 8.29 and 8.14 (N=C(H)-C'(H)=N), 7.2 - 7.1 (m, 6, H_{aryl}), 2.33 and 2.30 (s, 6 each, Ar, Ar': Me), 0.61 (s, 3, PdMe); 13 C NMR (CD₂Cl₂, 100 MHz, 41 °C) δ 165.1 (J_{CH} = 179.2, N=C(H)), 161.0 (J_{CH} = 177.8 (N=C'(H)), 147.3 and 146.6 (Ar, Ar': C_{ipso}), 129.5 and 128.8 (Ar, Ar': C_o), 128.8 and 128.5 (Ar, Ar': C_m), 127.9 and 127.3 (Ar, Ar': C_p), 18.7 and 18.2 (Ar, Ar': Me), 2.07 (J_{CH} = 136.4, PdMe).

Example 5

[4-MePh) DABMe, PdMeCl

Following the procedure of Example 1, a yellow powder was isolated in 92.1% yield: ¹H NMR (CD₂Cl₂, 5 400 MHz) δ 7.29 (d, 2, J = 8.55, Ar: H_m), 7.26 (d, 2, J = 7.83, Ar': H_m), 6.90 (d, 2, J = 8.24, Ar': H_o), 6.83 (d, 2, J = 8.34, Ar: H_o), 2.39 (s, 6, Ar, Ar': Me), 2.15 and 2.05 (s, 3 each, N=C(Me)-C'(Me)=N), 0.44 (s, 3, PdMe); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 176.0 and 169.9 (N=C-C'=N), 144.9 and 143.7 (Ar, Ar': C_{ipso}), 137.0 and 136.9 (Ar, Ar': C_p), 130.0 and 129.3 (Ar, Ar': C_m), 122.0 and 121.5 (Ar, Ar': C_o), 21.2 (N=C(Me)), 20.1 (Ar, Ar': Me), 19.8 (N=C'(Me)), 2.21 (J_{CH} = 135.3, PdMe). Anal. Calcd for (C₁₉H₂₃ClN₂Pd): C, 54.17; H, 5.50; N, 6.65. Found: C, 54.41; H, 5.37; N, 6.69.

Example 6

[(4-MePh)₂DABH₂]PdMeCl

Following the procedure of Example 1, a burnt orange powder was isolated in 90.5% yield: Anal. Calcd for (C₁₇H₁₉ClN₂Pd): C, 51.93; H, 4.87; N, 7.12. Found: C, 51.36; H, 4.80; N, 6.82.

Example 7

 $\langle \{ [(2,6-i-PrPh)_2DABMe_2] PdMe \}_2 (\mu-Cl) \rangle BAF^-$

Et₂O (25 mL) was added to a mixture of [(2,6-i-25 PrPh)₂DABMe₂]PdMeCl (0.81 g, 1.45 mmol) and 0.5 equiv of NaBAF (0.64 g, 0.73 mmol) at room temperature. A golden yellow solution and NaCl precipitate formed immediately upon mixing. The reaction mixture was stirred overnight and then filtered. After the Et₂O 30 was removed in vacuo, the product was washed with 25 mL of hexane. The yellow powder was then dissolved in 25 mL of CH₂Cl₂ and the resulting solution was filtered in order to removed traces of unreacted NaBAF. Removal of CH₂Cl₂ in vacuo yielded a golden yellow powder (1.25 g, 88.2%): ${}^{1}H$ NMR (CD₂Cl₂, 400 MHz) δ 7.73 (s, 8, BAF: 35 H_o), 7.57 (s, 4; BAF: H_p), 7.33 (t, 2, J = 7.57, Ar: H_p), 7.27 (d, 4, J = 7.69, Ar: H_o), 7.18 (t, 2, J = 7.64, Ar: H_p), 7.10 (d, 4, J = 7.44, Ar': H_o), 2.88

(septet, 4, J = 6.80, $CHMe_2$), 2.75 (septet, 4, J =6 82, $C'HMe_2$), 2.05 and 2.00 (s, 6 each, N=C(Me)-C'(Me) = N), 1.22, 1.13, 1.08 and 1.01 (d, 12 each, J =6.61-6.99, CHMeMe', C'HMeMe'), 0.41 (s, 6, PdMe); 13C NMR (CD₂Cl₂, 100 MHz) δ 177.1 and 171.2 (N=C-C'=N), 162.2 (q, $J_{BC} = 49.8$, BAF: C_{ipso}), 141.4 and 141.0 (Ar, Ar': C_{ipso}), 138.8 and 138.1 (Ar, Ar': C_o), 135.2 (BAF: C_p), 129.3 (q, J_{CF} = 31.6, BAF: C_m), 128.6 and 127.8 $(Ar, Ar': C_p)$, 125.0 $(q, J_{CF} = 272.5, BAF: CF_3)$, 124.5 10 and 123.8 (Ar, Ar': C_m), 117.9 (BAF: C_p), 29.3 (CHMe₂), 29.0 (C'HMe₂), 23.8, 23.7, 23.6 and 23.0 (CHMeMe', C'HMeMe'), 21.5 and 20.0 (N=C(Me)-C'(Me)=N), 9.8 (J_{CH} = 136.0, PdMe). Anal. Calcd for $(C_{90}H_{98}BClF_{24}N_4Pd_2)$: C, 55.41; H, 5.06; N, 2.87. Found: C, 55.83; H, 5.09; N, 15 2.63.

Example 8

 $\langle \{ [(2,6-i-PrPh),DABH_2] PdMe \}_2 (\mu-Cl) \rangle BAF^-$

The procedure of Example 7 was followed with one exception, the removal of CH2Cl2 in vacuo yielded a 20 product that was partially an oil. Dissolving the compound in Et₂O and then removing the Et₂O in vacuo yielded a microcrystalline red solid (85.5%): 1H NMR $(CD_2Cl_2, 400 \text{ MHz})$ δ 8.20 and 8.09 (s, 2 each, N=C(H)-C'(H) = N), 7.73 (s, 8, BAF: H_0), 7.57 (s, 4, BAF: H_p), 25 7.37 (t, 2, J = 7.73, Ar: H_p), 7.28 (d, 4, J = 7.44, Ar: H_m), 7.24 (t, 2, Ar': H_p), 7.16 (d, 4, J = 7.19, Ar': H_m), 3.04 (septet, 4, J = 6.80, $CHMe_2$), 2.93 (septet, 4, J = 6.80, $C'HMe_2$), 1.26 (d, 12, J = 6.79, CHMeMe'), 1.14 (d, 12, J = 6.83, CHMeMe'), 1.11 (d, 12, 30 J = 6.80, C'HMeMe'), 1.06 (d, 12, J = 6.79, C'HMeMe'), 0.74 (s, 6, PdMe); 13 C NMR (CD₂Cl₂ , 100 MHz) δ 166.0 $(J_{CH} = 180.4, N=C(H)), 161.9 (q, J_{BC} = 49.6, BAF)$ C_{ipso}), 160.8 ($J_{CH} = 179.9$, N=C'(H)), 143.5 and 143.0 $(Ar, Ar': C_{ipso})$, 139.8 and 138.9 $(Ar, Ar': C_o)$, 135.2 $(BAF: C_o)$, 129.3 $(q, J_{CF} = 31.4, BAF: C_m)$, 129.3 and 35 128.5 (Ar, Ar': C_p), 125.0 (q, $J_{CF} = 272.4$, BAF: CF_3), 124.3 and 123.7 (Ar, Ar': C_m), 117.9 (BAF: C_p), 29.2

and 28.9 (CHMe2, C'HMe2), 24.5, 24.1, 23.0, and 22.5

(CHMeMe', C'HMeMe'), 10.3 (PdMe). Anal. Calcd for $(C_{86}H_{90}BClF_{24}N_4Pd_2): \quad \text{C, 54.52; H, 4.97; N, 2.96.}$ Found: C, 54.97; H, 4.72; N, 2.71.

Example 9

Alternatively, the products of Examples 7 and 8 have been synthesized by stirring a 1:1 mixture of the appropriate PdMeCl compound and NaBAF in Et₂O for ~1 h. Removal of solvent yields the dimer + 0.5 equiv of Na+(OEt₂)₂BAF⁻. Washing the product mixture with 10 hexane yields ether-free NaBAF, which is insoluble in CH₂Cl₂. Addition of CH₂Cl₂ to the product mixture and filtration of the solution yields salt-free dimer: 1H NMR spectral data are identical with that reported above.

15 For a synthesis of CODPdMe₂, see: Rudler-Chauvin, M., and Rudler, H. J. Organomet. Chem. 1977, 134, 115-119.

Example 10

[(2,6-i-PrPh)₂DABMe₂]PdMe₂

A Schlenk flask containing a mixture of [(2,6-i-20 PrPh)₂DABMe₂]PdMeCl (2.00 g, 3.57 mmol) and 0.5 equiv of Me_2Mg (97.2 mg, 1.79 mmol) was cooled to -78 °C, and the reaction mixture was then suspended in 165 mL of Et₂O. The reaction mixture was allowed to warm to room temperature and then stirred for 2 h, and the resulting 25 brown solution was then filtered twice. Cooling the solution to -30 °C yielded brown single crystals (474.9 mg, 24.6%, 2 crops): ^{1}H NMR ($C_{6}D_{6}$, 400 MHz) δ 7.2-7.1 $(m, 6, H_{aryl}), 3.17 (septet, 4, J = 6.92, CHMe₂), 1.39$ (d, 12, J = 6.74, CHMeMe'), 1.20 (N=C(Me)-C(Me)=N),30 1.03 (d, 12, J = 6.89, CHMeMe'), 0.51 (s, 6, PdMe); ^{13}C NMR (C_6D_6 , 100 MHz) δ 168.4 (N=C-C=N), 143.4 (Ar: C_{ipso}), 138.0 (Ar: C_o), 126.5 (Ar: C_p), 123.6 (Ar: C_m), 28.8 ($CHMe_2$), 23.6 and 23.5 (CHMeMe'), 19.5 (N=C(Me)-C(Me)=N), -4.9 ($J_{CH}=127.9$, PdMe). Anal. Calcd for 35 $(C_{30}H_{46}N_{2}Pd)$: C, 66.59; H, 8.57; N, 5.18. Found: C, 66.77; H, 8.62; N, 4.91.

Example 11

[(2,6-i-PrPh)2DABH2]PdMe2

The synthesis of this compound in a manner analogous to Example 10, using 3.77 mmol of ArN=C(H) - C(H)=NAr and 1.93 mmol of Me₂Mg yielded 722.2 mg (37.4%) of a deep brown microcrystalline powder upon recrystallization of the product from a hexane/toluene solvent mixture.

This compound was also synthesized by the following method: A mixture of Pd(acac)₂ (2.66 g, 8.72 10 mmol) and corresponding diimine (3.35 g, 8.90 mmol) was suspended in 100 mL of Et₂O, stirred for 0.5 h at room temperature, and then cooled to -78°C. A solution of Me_2Mg (0.499 g, 9.18 mmol) in 50 mL of Et_2O was then 15 added via cannula to the cold reaction mixture. stirring for 10 min at -78°C, the yellow suspension was allowed to warm to room temperature and stirred for an additional hour. A second equivalent of the diimine was then added to the reaction mixture and stirring was 20 continued for ~4 days. The brown Et₂O solution was then filtered and the solvent was removed in vacuo to yield a yellow-brown foam. The product was then extracted with 75 mL of hexane; and the resulting solution was filtered twice, concentrated, and cooled to -30°C overnight to yield 1.43 g (32.0%) of brown 25 powder: ¹H NMR (C_6D_6 , 400 MHz) δ 7.40 (s, 2, N=C(H) -C(H)=N), 7.12 (s, 6, H_{aryl}), 3.39 (septet, 4, J=6.86, $CHMe_2$), 1.30 (d, 12, J = 6.81, CHMeMe'), 1.07 (d, 12, J = 6.91, CHMeMe'), 0.77 (s, 6, PdMe); 13 C NMR (C6D₆, 100 MHz) δ 159.9 (J_{CH} = 174.5, N=C(H)-C(H)=N), 145.7 (Ar: C_{ipso}), 138.9 (Ar: C_o), 127.2 (Ar: C_p), 123.4 (Ar: C_m), $28.5 \ (CHMe_2), 24.4 \ and 22.8 \ (CHMeMe'), -5.1 \ (J_{CH} =$ 128.3, PdMe). Anal. Calcd for $(C_{28}H_{42}N_2Pd)$: C, 65.55, H, 8.25; N, 5.46. Found: C, 65.14; H, 8.12; N, 5.14.

Example 12

[(2,6-MePh)2DABH2]PdMe2

This compound was synthesized in a manner similar to the second procedure of Example 11 (stirred for 5 h at rt) using 5.13 mmol of the corresponding diimine and 2.57 mmol of Me₂Mg. After the reaction mixture was filtered, removal of Et₂O in vacuo yielded 1.29 g (62.2%) of a deep brown microcrystalline solid: 1 H NMR (C₆D₆, 100 MHz, 12°C) δ 6.98 (s, 2, N=C(H)-C(H)=N), (0.95 (s, 6, H_{aryl}), 2.13 (s, 12, Ar: Me), 0.77 (s, 6, PdMe); 13 C NMR (C₆D₆, 400 MHz, 12°C) δ 160.8 (J_{CH} = 174.6, N=C(H)-C(H)=N), 147.8 (Ar: C_{ipso}), 128.2 (Ar: C_m), 128.15 (Ar: C_o), 126.3 (Ar: C_p), 18.2 (Ar: Me), -5.5 (J_{CH} = 127.6, Pd-Me).

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Example 13

[(2,6-i-PrPh)2DABH2]NiMe2

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. J. Organomet. Chem. 1980, 191, 321-328) and was modified as follows: A mixture 20 of Ni(acac)₂ (1.89 g, 7.35 mmol) and the corresponding diimine (2.83 q, 7.51 mmol) was suspended in 75 mL of Et₂O and the suspension was stirred for 1 h at room temperature. After cooling the reaction mixture to -78 °C, a solution of Me_2Mg (401 mg, 7.37 mmol) in 25 mL 25 of Et₂O was added via cannula. The reaction mixture was stirred for 1 h at -78°C and then for 2 h at 0°C to give a blue-green solution. After the solution was filtered, the Et₂O was removed in vacuo to give a bluegreen brittle foam. The product was then dissolved in 30 hexane and the resulting solution was filtered twice, concentrated, and then cooled to -30°C to give 1.23 g (35.9%, one crop) of small turquoise crystals.

Example 14

[(2,6-i-PrPh),DABMe,]NiMe,

The synthesis of this compound has been reported (Svoboda, M.; tom Dieck, H. J. Organomet. Chem. 1980, 191, 321-328) and was synthesized according to the above modified procedure (Example 13) using Ni(acac)₂

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(3.02 g, 11.75 mmol), the corresponding dimmine 74.80 g, 11.85 mmol) and Me₂Mg (640 mg, 11.77 mmol). A turquoise powder was isolated (620 mg, 10.7%).

Example 15

5 {[(2,6-MePh)₂DABMe₂]PdMe(MeCN)}BAF

To a mixture of [(2,6-MePh)₂DABMe₂]PdMeCl (109.5 mg, 0.244 mmol) and NaBAF (216.0 mg, 0.244 mmol) were added 20 mL each of Et₂O and CH₂Cl₂ and 1 mL of CH₃CN. The reaction mixture was then stirred for 1.5 h and then the NaCl was removed via filtration. Removal of the solvent in vacuo yielded a yellow powder, which was washed with 50 mL of hexane. The product (269.6 mg, 83.8%) was then dried in vacuo: 1H NMR (CD₂Cl₂, 400 MHz) δ 7.73 (s, 8, BAF: H_o), 7.57 (s, 4, BAF: H_p), 7.22-7.16 (m, 6, H_{aryl}), 2.23 (s, 6, Ar: Me), 2.17 (s, 6, Ar': Me), 2.16, 2.14, and 1.79 (s, 3 each, N=C(Me)-C'(Me) = N, NCMe), 0.38 (s, 3, PdMe); ¹³C NMR (CD_2Cl_2 , 100 MHz) δ 180.1 and 172.2 (N=C-C'=N), 162.1 (q, J_{BC} = 49.9, BAF: Cipso), 142.9 (Ar, Ar': Co), 135.2 (BAF: Co), 129.3 (Ar: C_m), 129.2 (q, $J_{CF} = 30.6$, BAF: C_m), 129.0 $(Ar': C_m)$, 128.4 $(Ar: C_p)$, 128.2 $(Ar: C_o)$, 127.7 $(Ar': C_o)$ C_p), 127.4 (Ar': C_o), 125.0 (q, $J_{CF} = 272.4$, BAF: CF_3), 121.8 (NCMe), 117.9 (BAF: C_p), 20.2 and 19.2 (N=C(Me)-C'(Me)=N), 18.0 (Ar: Me),17.9 (Ar': Me), 5.1 and 2.3 (NCMe, PdMe). Anal. Calcd for (C55H42BF24N3Pd): C, 50.12; H, 3.21; N, 3.19. Found: C, 50.13; H, 3.13, N,

Example 16

[(4-MePh) 2DABMe2] PdMe (MeCN) }BAF

Following the procedure of Example 15, a yellow powder was isolated in 85% yield: ^{1}H NMR (CD₂Cl₂, 400 MHz) δ 7.81 (s, 8, BAF: H_o), 7.73 (s, 4, BAF: H_p), 7.30 (d, 4, J = 8.41, Ar, Ar': H_m), 6.89 (d, 2, J = 8.26, Ar: H_o), 6.77 (d, 2, J = 8.19, Ar': H_o), 2.39 (s, 6, 35 Ar, Ar': Me), 2.24, 2.17 and 1.93 (s, 3 each, N=C(Me) - C'(Me)=N, NCMe)Pd-Me; ^{13}C NMR (CD₂Cl₂, 100 MHz) δ 180.7 and 171.6 (N=C-C'=N), 162.1 (q, J_{BC} = 49.8, BAF: C_{ipso}), 143.4 and 142.9 (Ar, Ar': C_{ipso}), 138.6 and 138.5 (Ar,

Ar': C_p), 135.2 (BAF: C_o), 130.6 and 130.4 (Ar, Ar': C_m), 129.3 (q, J_{CF} = 31.6, BAF: C_m), 125.0 (q, J_{CF} = 272.5, BAF: C_{F}), 122.1 (NCMe), 121.0 and 120.9 (Ar, Ar': C_o), 117.9 (BAF: C_p), 21.5 (ArN=C(Me)), 21.1 (Ar, Ar': Me), 19.7 (ArN=C'(Me)), 6.2 and 3.0 (NCMe, PdMe). Anal. Calcd for ($C_{53}H_{38}BF_{24}N_{3}Pd$): C_{7} , 49.34; H_{7} , 2.97: N_{7} , 3.26. Found: C_{7} , 49.55; C_{7} , 130.6 and 130.4 (Ar, Ar': C_{7}), 3.10.

Example 17

[(2,6-MePh)₂DABMe₂]PdMe(Et₂O)BAF

10 A Schlenk flask containing a mixture of [(2,6-i-PrPh)₂DABMe₂] PdMe₂ (501 mg, 0.926 mmol) and $H^+(OEt_2)_2BAF^-$ (938 mg, 0.926 mmol) was cooled to -78°C. Following the addition of 50 mL of Et₂O, the solution was allowed to warm and stirred briefly (~15 min) at 15 room temperature. The solution was then filtered and the solvent was removed in vacuo to give a pale orange powder (1.28 g, 94.5%), which was stored at -30°C under an inert atmosphere: ¹H NMR (CD₂Cl₂, 400 MHz, -60 °C) δ 7.71 (s, 8, BAF: H_o), 7.58 (s, 4, BAF: H_p), 7.4 - 7.0 20 $(m, 6, H_{aryl}), 3.18 (q, 4, J = 7.10, O(CH_2CH_3)_2), 2.86$ $(septet, 2, J = 6.65, CHMe_2), 2.80 (septet, 2, J =$ 6.55, $C'HMe_2$), 2.18 and 2.15 (N=C(Me)-C'(Me)=N), 1.34, 1.29, 1.14 and 1.13 (d, 6 each, J = 6.4-6.7, CHMeMe', C'HMeMe'), 1.06 (t, J = 6.9, $O(CH_2CH_3)_2$), 0.33 (s, 3, 25 PdMe); 13 C NMR (CD₂Cl₂, 100 MHz, -60°C) δ 179.0 and 172.1 (N=C-C'=N), 161.4 $(q, J_{BC} = 49.7, BAF: C_{ipso})$, 140.21 and 140.15 (Ar, Ar': Cipso), 137.7 and 137.4 $(Ar, Ar': C_0), 134.4 (BAF: C_p), 128.3 (q, J_{CF} = 31.3,$ BAF: C_m), 128.5 and 128.2 (Ar, Ar': C_p), 124.2 (q, J_{CF} 30 = 272.4, BAF: CF₃), 117.3 (BAF: C_D), 71.5 (O(CH₂CH₃)₂), $28.7 \ (CHMe_2), \ 28.4 \ (C'HMe_2), \ 23.7, \ 23.6, \ 23.1 \ and \ 22.6$ (CHMeMe', C'HMeMe'), 21.5 and 20.7 (N=C(Me)-C'(Me)=N),14.2 (O(CH₂CH₃)₂)₂, 8.6 (PdMe). Anal. Calcd for $(C_{65}H_{65}BF_{24}N_{2}OPd)$: C, 53.35; H, 4.48; N, 1.91. Found: 35 C, 53.01; H, 4.35; N, 1.68.

Example 18

[(2,6-MePh)2DABH2]PdMe(Et2O)BAF

Following the procedure of Example 17, an orange powder was synthesized in 94.3% yield and stored at -¹H NMR (CD₂Cl₂, 400 MHz, -60°C) δ 8.23 and 8.20 30°C: (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, $BAF: H_O$), 7.54 $(s, 4, BAF: H_p), 7.40 - 7.27 (m, 6, H_{arv1}), 3.32 (q, 4)$ J = 6.90, $O(CH_2CH_3)_2$, 3.04 and 3.01 (septets, 2 each, J = 6.9 - 7.1, $CHMe_2$ and $C'HMe_2$), 1.32, 1.318, 1.14 and 10 1.10 (d, 6 each, J = 6.5 - 6.8, CHMeMe' and C'HMeMe'), 1.21 (t, 6, J = 6.93, $O(CH_2CH_3)_2$), 0.70 (s, 3, PdMe); ¹³C NMR (CD₂Cl₂, 100 MHz, -60°C) δ 166.9 (J_{CH} = 182.6, N=C(H)), 161.5 ($J_{BC} = 49.7$, BAF: C_{ipso}), 161.3 ($J_{CH} = 49.7$) 181.6, N=C'(H)), 143.0 and 141.8 (Ar, Ar': C_{ipso}), 15 138.7 and 137.8 (Ar, Ar': C_o), 134.4 (BAF: C_o), 129.1 and 128.8 (Ar, Ar': C_p), 128.3 ($J_{CF} = 31.3$, BAF: C_m), 124.0 and 123.9 (Ar, Ar': C_m), 117.3 (BAF: C_p), 72.0 $(O(CH_2CH_3)_2)$, 28.5 and 28.4 $(CHMe_2, C'HMe_2)$, 25.2, 24.1, 21.9 and 21.7 (CHMeMe', C'HMeMe'), 15.2 (O(CH_2CH_3)₂), 20 11.4 $(J_{CH} = 137.8, PdMe)$. Anal. Calcd for $(C_{63}H_{61}BF_{24}N_{2}OPd)$: C, 52.72; H, 4.28; N, 1.95. Found: C, 52.72; H, 4.26; N, 1.86.

Example 19

[(2,6-MePh),DABMe,]NiMe(Et,O)BAF

25 Following the procedure of Example 17, a magenta powder was isolated and stored at -30°C: 1H NMR (CD₂Cl₂, 400 MHz, -60°C; A H₂O adduct and free Et₂O were observed.) δ 7.73 (s, 8, BAF: H_0), 7.55 (s, 4, BAF: H_D), 7.4 - 7.2 (m, 6, H_{arvl}), 3.42 (s, 2, OH_2), 3.22 (q, 4, $O(CH_2CH_3)_2$), 3.14 and 3.11 (septets, 2 30 each, J = 7.1, $CHMe_2$, $C'HMe_2$), 1.95 and 1.78 (s, 3) each, N=C(Me)-C'(Me)=N), 1.42, 1.39, 1.18 and 1.11 (d, 6 each, J = 6.6 - 6.9, CHMeMe' and C'HMeMe'), 0.93 (t, J = 7.5, $O(CH_2CH_3)_2$, -0.26 (s , 3, NiMe); ¹³C NMR $(CD_2Cl_2 \ 100 \ MHz, -58^{\circ}C) \ \delta \ 175.2 \ and \ 170.7 \ (N=C-C'=N),$ 161.6 (q, $J_{BC} = 49.7$, BAF: C_{ipso}), 141.2 (Ar: C_{ipso}), 139.16 and 138.68 (Ar, Ar': Co), 136.8 (Ar': Cipso), 134.5 (BAF: C_0), 129.1 and 128.4 (Ar, Ar': C_p), 128.5

 $(q, J_{CF} = 32.4, BAF: C_m)$, 125.0 and 124.2 (Ar, Ar': C_m), 124.3 $(q, J_{CF} = 272.5, BAF: CF_3)$, 117.4 $(BAF: C_p)$, 66.0 $(O(CH_2CH_3)_2)$, 29.1 $(CHMe_2)$, 28.9 $(C'HMe_2)$, 23.51, 23.45, 23.03, and 22.95 (CHMeMe', C'HMeMe'), 21.0 and 19.2 (N=C(Me)-C'(Me)=N), 14.2 $(OCH_2CH_3)_2)$, -0.86 $(J_{CH} = 131.8, NiMe)$. Anal. Calcd for $(C_{65}H_{65}BF_{24}N_2NiO)$: C, 55.15; H, 4.63; N, 1.98. Found: C, 54.74; H, 4.53; N, 2.05.

Example 20

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[-(2,6-MePh)2DABH2] NiMe (Et2O) BAF

Following the procedure of Example 17, a purple powder was obtained and stored at -30°C: ¹H NMR (CD₂Cl₂, 400 MHz, -80°C; H₂O and Et₂O adducts were observed in an 80:20 ratio, respectively.) δ 8.31 and 8.13 (s, 0.8 each, N=C(H)-C'(H)=N; H₂O Adduct), 8.18 and 8.00 (s, 0.2 each, N=C(H)-C'(H)=N; Et₂O Adduct), 7.71 (s, 8 BAF: C_o), 7.53 (s, 4, BAF: C_p), 7.5 - 7.0 (m, 6, H_{aryl}), 4.21 (s, 1.6, OH₂), 3.5 - 3.1 (m, 8, O(CH₂CH₃)₂, CHMe₂, C'HMe₂), 1.38, 1.37, 1.16 and 1.08 (d, 4.8 each, CHMeMe', C'HMeMe'; H₂O Adduct; These peaks overlap with and obscure the CHMe₂ doublets of the Et₂O adduct.), 0.27 (s, 2.4, PdMe; H₂O Adduct), 0.12 (s, 0.6, PdMe: Et₂O Adduct).

Examples 21-23

25 The rate of exchange of free and bound ethylene was determined by 'H NMR line broadening experiments at -85°C for complex (XI), see the Table below. instrument was a 400 MHz Varian® NMR spectrometer. Samples were prepared according to the following 30 procedure: The palladium ether adducts {[(2,6-i- $PrPh)_2DABMe_2$ PdMe (OEt₂) BAF, { [(2,6-i- $PrPh)_2An]PdMe(OEt_2)BAF$, and {[(2,6-i-PrPh) 2DABH2] PdMe (OEt2) BAF were used as precursors to (XI), and were weighed (~15 mg) in a tared 5 mm dia. 35 NMR tube in a nitrogen-filled drybox. The tube was then capped with a septum and Parafilm® and cooled to -80°C. Dry, decassed CD₂Cl₂ (700 μ L) was then added to the palladium complex via gastight syringe, and the

homogeneous solution. After acquiring a -85°C NMR spectrum, ethylene was added to the solution via gastight syringe and a second NMR spectrum was acquired at -85°C. The molarity of the BAF counterion was calculated according to the moles of the ether adduct placed in the NMR tube. The molarity of (XI) and free ethylene were calculated using the BAF peaks as an internal standard. Line-widths (W) were measured at half-height in units of Hz for the complexed ethylene signal (usually at 5 to 4 ppm) and were corrected for line widths (W₀) in the absence of exchange.

For (XI) the exchange rate was determined from the standard equation for the slow exchange approximation:

$$k = (W - W_0) \pi / [=],$$

where [=] is the molar concentration of ethylene. These experiments were repeated twice and an average value is reported below.

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Rate Constants for Ethylene Exchangea

Ex.	(XI)	k (L-M ⁻¹ s ⁻¹)
21	{[(2,6-i-PrPh)2DABMe2]PdMe(=)}BAF	45
22	{ [(2,6-i-PrPh)2An] PdMe(=) }BAF	520
23	{ [(2,6-i-PrPh)2DABH2] PdMe(=)}BAF	8100

 $^{\mathrm{a}}$ The T_{1} of free ethylene is 15 sec. A pulse delay of 60 sec and a 30° pulse width were used.

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Example 24

Anhydrous FeCl₂ (228 mg, 1.8 mmol) and (2,6-i-PrPh)₂DABAn (1.0 g, 2.0 mmol) were combined as solids and dissolved in 40 ml of CH_2Cl_2 . The mixture was stirred at 25°C for 4 hr. The resulting green solution was removed from the unreacted FeCl₂ via filter cannula. The solvent was removed under reduced

pressure resulting in a green solid (0.95 g, 84% yield).

A portion of the green solid (40 mg) was immediately transferred to another Schlenk flask and dissolved in 50 ml of toluene under 1 atm of ethylene. The solution was cooled to 0°C, and 6 ml of a 10% MAO solution in toluene was added. The resulting purple solution was warmed to 25°C and stirred for 11 hr. The polymerization was quenched and the polymer precipitated by acetone. The resulting polymer was washed with 6M HCl, water and acetone. Subsequent drying of the polymer resulted in 60 mg of white polyethylene. 1 H NMR (CDCl₃, 200 MHz) δ 1.25 (CH₂, CH) δ 0.85 (m, CH₃).

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Example 25

(2-t-BuPh) 2DABMe2

A Schlenk tube was charged with 2-t-butylaniline (5.00 mL, 32.1 mmol) and 2,3-butanedione (1.35 mL, 15.4 mmol). Methanol (10 mL) and formic acid (1 mL) were 20 added and a yellow precipitate began to form almost immediately upon stirring. The reaction mixture was allowed to stir overnight. The resulting yellow solid was collected via filtration and dried under vacuum. The solid was dissolved in ether and dried over NapSO4 for 2-3 h. The ether solution was filtered, condensed 25 and placed into the freezer (-30°C). Yellow crystals were isolated via filtration and dried under vacuum overnight (4.60 g, 85.7%): 1 H NMR (CDCl₃, 250 MHz) δ 7.41 (dd, 2H, J = 7.7, 1.5 Hz, H_m), 7.19 (td, 2H, J = 7.5, 30 1.5 Hz, H_m or H_p), 7.07 (td, 2H, J = 7.6, 1.6 Hz, H_m or H_D), 6.50 (dd, 2H, J = 7.7, 1.8 Hz, H_O), 2.19 (s, 6H, N=C(Me)-C(Me)=N), 1.34 (s, 18H, $C(CH_3)_3$).

Examples 26 and 27

General Polymerization Procedure for Examples 26 and 27: In the drybox, a glass insert was loaded with $[(\eta^3-C_3H_5)Pd(\mu-Cl)]_2$ (11 mg, 0.03 mmol), NaBAF (53 mg, 0.06 mmol), and an α -diimine ligand (0.06 mmol). The insert was cooled to -35°C in the drybox freezer, 5 mL

of C_6D_6 was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a ^1H NMR spectrum. The remaining portion was added to ^2O mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum

Example 26

10 α -Diimine was $(2,6-i-PrPh)_2DABMe_2$. Polyethylene (50 mg) was isolated as a solid. ¹H NMR spectrum (C_6D_6) is consistent with the production of 1- and 2-butenes and branched polyethylene.

Example 27

15 α -Diimine was $(2,6-i-PrPh)_2DABAn$. Polyethylene (17 mg) was isolated as a solid. ¹H NMR spectrum (C_6D_6) is consistent with the production of branched polyethylene.

Example 28

20 [(2,6-i-PrPh)₂DABH₂]NiBr₂

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The corresponding diimine (980 mg, 2.61 mmol) was dissolved in 10 mL of CH_2Cl_2 in a Schlenk tube under a N_2 atmosphere. This solution was added via cannula to a suspension of (DME) $NiBr_2$ (DME = 1,2-dimethoxyethane) (787 mg, 2.55 mmol) in CH_2Cl_2 (20 mL). The resulting red/brown mixture was stirred for 20 hours. The solvent was evaporated under reduced pressure resulting in a red/brown solid. The product was washed with 3 x 10 mL of hexane and dried in vacuo. The product was isolated as a red/brown powder (1.25 g, 82% yield).

Example 29

[(2,6-i-PrPh),DABMe,]NiBr,

Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) (DME) NiBr $_2$ and 687 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as an orange/brown powder (670 mg, 67% yield).

Example 30

[(2,6-MePh)₂DABH₂]NiBr₂

Using a procedure similar to that of Example 28, 500 mg (1.62 mmol) (DME)NiBr₂ and 448 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as a brown powder (622 mg, 80% yield).

Example 31

[(2,6-i-PrPh)2DABAn]NiBr2

Using a procedure similar to that of Example 28, 10 500 mg (1.62 mmol) (DME)NiBr₂ and 850 mg (1.70 mmol) of the corresponding diimine were combined. The product was isolated as a red powder (998 mg, 86% yield). Anal. Calcd. for C₃₆H₄₀N₂Br₂Ni: C, 60.12; H, 5.61; N, 3.89. Found C, 59.88; H, 5.20; N, 3.52.

15 Example 32

[(2,6-MePh)2DABAn]NiBr2

The corresponding diimine (1.92 g, 4.95 mmol) and (DME)NiBr₂ (1.5 g, 4.86 mmol) were combined as solids in a flame dried Schlenk under an argon atmosphere. To this mixture 30 mL of CH₂Cl₂ was added giving an orange solution. The mixture was stirred for 18 hours resulting in a red/brown suspension. The CH₂Cl₂ was removed via filter cannula leaving a red/brown solid. The product was washed with 2 x 10 mL of CH₂Cl₂ and dried under vacuum. The product was obtained as a red/brown powder (2.5 g, 83% yield).

Example 33

[(2,6-MePh)2DABMe2]NiBr2

Using a procedure similar to that of Example 32, the title compound was made from 1.5 g (4.86 mmol) (DME)NiBr₂ and 1.45 g (4.95 mmol) of the corresponding diimine. The product was obtained as a brown powder (2.05 g, 81% yield).

Example 34

35 [(2,6-i-PrPh)₂DABMe₂]PdMeCl

(COD) PdMeCl (9.04 g, 34.1 mmol) was dissolved in 200 ml of methylene chloride. To this solution was added the corresponding dimine (13.79 g, 34.1 mmol).

The resulting solution rapidly changed color from yellow to orange-red. After stirring at room temperature for several hours it was concentrated to form a saturated solution of the desired product, and cooled to -40°C overnight. An orange solid crystallized from the solution, and was isolated by filtration, washed with petroleum ether, and dried to afford 12.54 g of the title compound as an orange powder. Second and third crops of crystals obtained from the mother liquor afforded an additional 3.22 g of product. Total yield = 87%.

Examples 35-39

The following compounds were made by a method similar to that used in Example 34.

13		•
	Example	Compound
	35	[(2,6-i-PrPh)2DABH2]PdMeCl
	36 ,	[(2,6-i-PrPh) ₂ DABAn]PdMeCl
	37	[(Ph)2DABMe2]PdMeCl
20	38	[(2,6-EtPh) ₂ DABMe ₂]PdMeCl
	39	[(2,4,6-MePh),DABMe,]PdMeCl

Note: The diethyl ether complexes described in Examples 41-46 are unstable in non-coordinating 25 solvents such as methylene chloride and chloroform. They are characterized by ¹H NMR spectra recorded in CD3CN; under these conditions the acetonitrile adduct of the Pd methyl cation is formed. Typically, less than a whole equivalent of free diethylether is observed by 1H NMR when [(R)2DAB(R')2]PdMe(OEt2)X is 30 dissolved in CD3CN. Therefore, it is believed the complexes designated as "{[(R)2DAB(R')2]PdMe(OEt2)}X" below are likely mixtures of ${[(R)_2DAB(R')_2]PdMe(OEt_2)}X$ and $[(R)_2DAB(R')_2]PdMeX$, and in the latter complexes the X ligand (SbF6, BF4, or PF6) is weakly coordinated to palladium. A formula of the type $\{(R)_2DAB(R')_2\}PdMe(OEt_2)\}X''$ is a "formal" way of conveying the approximate overall composition of

chis compound, but may not accurately depict the exact coordination to the metal atom.

Listed below are the ^{13}C NMR data for Example 36.

5 13C NMR data

TCB,	120C,	0.05M	CrAcAc

	ICB,	120C, 0.05M CIACAC
freq ppm	intensity	
46.5568	24.6005	1 cmp and/or 1,3 ccmcc
44.9321	3.42517	1,3 cmc
40.8118	55.4341	2 pmp
40.3658	145.916	1,3 pmp
39.5693	18.458	methylenes from 2 cmp and/or 2 cmc
38.7782	4.16118	
38.6295	5.84037	
38.2844	8.43098	•
38.1198	8.29802	
37.8384	3.83966	
37.5198	13.4977	
37.2384	23.4819	
37.1163	16.8339	•
36.7446	114.983	
36.0012	6.19217	
35.7198	5.17495	
34.2278	4.83958	
32.9216	20.2781	3B ₆ ⁺ , 3EOC
32.619	3.6086	
32.4172	2.98497	
32.1995	10.637	
31.9765	42.2547	•
31.8809	143.871	
30.4686	27.9974	·
30.3199	47.1951	
30.0225	36.1409	•
29.7411	102.51	
29.311	4.83244	
28.7111	117.354	
28.2597	9.05515	
27.1659	22.5725	
27.0067	5.81855	
26.1146	13.5772	00-B
24.5642	2.59695	ββВ ^В
22.6368	12.726	2B ₅ ⁺ , 2EOC
20.1413	3.7815	2B ₃
19.7271	20.0959	1B ₁
17.5236	7.01554	end group
14.2528	3.03535	1B ₃ 1B ₄ +, 1EOC
13.8812	12.3635	164 , 120C

Example 40

 ${ [(4-Me_2NPh)_2DABMe_2] PdMe(MeCN) } SbF_5\cdot MeCN$

A procedure analogous to that used in Example 54, using $(4-\text{Me}_2\text{NPh})_2\text{DABMe}_2$ in place of $(2-\text{C}_6\text{H}_4-\text{tBu})_2\text{DABMe}_2$, afforded $\{[(4-\text{NMe}_2\text{Ph})_2\text{DABMe}_2]\text{PdMe}(\text{MeCN})\}\text{SbF}_6\text{-MeCN}$ as a purple solid (product was not recrystallized in this instance). ¹H NMR (CD_2Cl_2) δ 6.96 (d, 2H, H_{aryl}), 6.75 (mult, 6H, H_{aryl}), 3.01 (s, 6H, NMe₂), 2.98 (s, 6H, NMe'₂), 2.30, 2.18, 2.03, 1.96 (s's, 3H each, N=CMe, N=CMe', and free and coordinated N=CMe), 0.49 (s, 3H, Pd-Me).

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Example 41

 $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)_n\}SbF_6$ [(2,6-i-PrPh),DABMe,]PdMeCl (0.84 g, 1.49 mmol) was suspended in 50 mL of diethylether and the mixture cooled to -40° C. To this was added AgSbF₆ (0.52 g, 1.50 mmol). The reaction mixture was allowed to warm 15 to room temperature, and stirred at room temperature for 90 min. The reaction mixture was then filtered, giving a pale yellow filtrate and a bright yellow precipitate. The yellow precipitate was extracted with 20 4 x 20 mL 50/50 methylene chloride/diethyl ether. filtrate and extracts were then combined with an additional 30 mL diethyl ether. The resulting solution was then concentrated to half its original volume and 100 mL of petroleum ether added. The resulting precipitate was filtered off and dried, affording 1.04 25 g of the title compound as a yellow-orange powder (83% yield). ¹H NMR (CD₃CN) δ 7.30 (mult, 6H, H_{aryl}), 3.37 [q, free $O(CH_2CH_3)_2$], 3.05-2.90 (overlapping sept's, 4H, $CHMe_2$), 2.20 (s, 3H, N=CMe), 2.19 (s, 3H, $N=CMe^4$), 1.35-1.14 (overlapping d's, 24H, CHMe2), 1.08 (t, free 30 $O(CH_2CH_3)_2$, 0.28 (s, 3H, Pd-Me). This material contained 0.4 equiv of Et₂O per Pd, as determined by ¹H NMR integration.

Example 42

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 $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)_n\}BF_4$

A procedure analogous to that used in Example 41, using $AgBF_4$ in place of $AgSbF_6$, afforded the title compound as a mustard yellow powder in 61% yield. This

material contained 0.3 equiv of Et₂O per Pd, as determined by ¹H NMR integration. ¹H NMR in CD₃CN was otherwise identical to that of the compound made in Example 41.

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Example 43

 $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)_n\}PF_6^{-1}$

A procedure analogous to that used in Example 41, using AgPF₆ in place of AgSbF₆, afforded the title compound as a yellow-orange powder in 72% yield. This material contained 0.4 equiv of Et₂O per Pd, as determined by ¹H NMR integration. ¹H NMR in CD₃CN was identical to that of the compound of Example 41.

Example 44

 $\{ [(2,6-i-PrPh)_2DABH_2] PdMe (Et_2O)_n \} SbF_6^{-1}$

A procedure analogous to that used in Example 41, using $[(2,6-i-PrPh)_2DABH_2]PdMeCl$ in place of $[(2,6-i-PrPh)_2DABMe_2]PdMeCl$, afforded the title compound in 71% yield. 1H NMR (CD_3CN) δ 8.30 (s, 2H, N=CH and N=CH'), 7.30 (s, 6H, H_{aryl}), 3.37 [q, free $O(CH_2CH_3)_2$], 3.15 (br, 4H, $CHMe_2$), 1.40-1.10 (br, 24H, $CHMe_2$), 1.08 (t, free $O(CH_2CH_3)_2$], 0.55 (s, 3H, Pd-Me). This material contained 0.5 equiv of Et₂O per Pd, as determined by 1H NMR integration.

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Example 45

 $\{[(2,4,6-MePh)_2DABMe_2]PdMe(Et_2O)_n\}SbF_6\}$

[(2,4,6-MePh)₂DABMe₂]PdMeCl (0.50 g, 1.05 mmol) was partially dissolved in 40 mL 50/50 methylene chloride/diethylether. To this mixture at room temperature was added AgSbF₆ (0.36 g, 1.05 mmol). The resulting reaction mixture was stirred at room temperature for 45 min. It was then filtered, and the filtrate concentrated in vacuo to afford an oily solid. The latter was washed with diethyl ether and dried to afford the title compound as a beige powder. ¹H NMR (CD₃CN) δ 6.99 (s, 4H, H_{aryl}), 3.38 [q, free O(CH₂CH₃)₂], 2.30-2.00 (overlapping s's, 24H, N=CMe, N=CMe' and aryl Me's), 1.08 (t, free O(CH₂CH₃)₂], 0.15

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is, 3H, Pd-Me). This material contained 6:7 equiv of Et₂O per Pd, as determined by $^1\mathrm{H}$ MR integration.

Example 46

 $\{[(2,6-i-PrPh)_2DABAn]PdMe(Et_2O)_n\}SbF_6^-$

A procedure analogous to that used in Example 41, using [(2,6-i-PrPh)₂DABAn]PdMeCl in place of [(2,6-i-PrPh)₂DABMe₂]PdMeCl, afforded the title compound in 92% yield. ¹H NMR (CD₃CN) δ 8.22 (br t, 2H, H_{aryl}), 7.60-7.42 (br mult, 8H, H_{aryl}), 6.93 (br d, 1H, H_{aryl}), 6.53 (br d, 1H, H_{aryl}), 3.38 [q, free O(CH₂CH₃)₂], 3.30 (br mult, 4H, CHMe₂), 1.36 (br d, 6H, CHMe₂), 1.32 (br d, 6H, CHMe₂), 1.08 (t, free O(CH₂CH₃)₂], 1.02 (br d, 6H, CHMe₂), 0.92 (br d, 6H, CHMe₂), 0.68 (s, 3H, Pd-Me). The amount of ether contained in the product could not be determined precisely by ¹H NMR integration, due to overlapping resonances.

Example 47

[(2,6-i-PrPh)2DABMe2]PdMe(OSO2CF3)

A procedure analogous to that used in Example 41, using $AgOSO_2CF_3$ in place of $AgSbF_6$, afforded the title compound as a yellow-orange powder. ¹H NMR in CD_3CN was identical to that of the title compound of Example 41, but without free ether resonances.

Example 48

25 { [(2,6-i-PrPh) 2DABMe2] PdMe(MeCN) }SbF6 [(2,6-i-PrPh)₂DABMe₂]PdMeCl (0.40 g, 0.71 mmol) was dissolved in 15 mL acetonitrile to give an orange solution. To this was added AgSbF₆ (0.25 g, 0.71 mmol) at room temperature. AgCl immediately precipitated from the resulting bright yellow reaction mixture. 30 mixture was stirred at room temperature for 3 h. It was then filtered and the AgCl precipitate extracted with 5 mL of acetonitrile. The combined filtrate and extract were concentrated to dryness affording a yellow solid. This was recrystallized from methylene chloride/petroleum ether affording 0.43 g of the title compound as a bright yellow powder (Yield = 75%). NMR (CDCl₃) δ 7.35-7.24 (mult, 6H, H_{aryl}), 2.91 (mult,

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4H, $CHMe_2$), 2.29 (s, 3H, N=CMe), 2.28 (s, 3H, $N=CMe^{-1}$), 1.81 (s, 3H, N=CMe), 1.37-1.19 (overlapping d's, 24H, $CHMe^{-1}$ s), 0.40 (s, 3H, Pd-Me). This compound can also be prepared by addition of acetonitrile to {[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)}SbF₆

Example 49

{ [(Ph)₂DABMe₂] PdMe (MeCN) }SbF₆

A procedure analogous to that used in Example 48, using [(Ph)₂DABMe₂]PdMeCl in place of [(2,6-i10 PrPh)₂DABMe₂]PdMeCl, afforded the title compound as a yellow microcrystalline solid upon recrystallization from methylene chloride / petroleum ether. This complex crystallizes as the acetonitrile solvate from acetonitrile solution at -40°C. ¹H NMR of material recrystallized from methylene chloride/petroleum ether: (CDCl₃) δ 7.46 (mult, 4H, H_{aryl}), 7.30 (t, 2H, H_{aryl}), 7.12 (d, 2H, H_{aryl}), 7.00 (d, 2H, H_{aryl}), 2.31 (s, 3H, N=CMe), 2.25 (s, 3H, N=CMe⁺), 1.93 (s, 3H, N≡CMe), 0.43 (s, 3H, Pd-Me).

20 Example 50

{ [(2,6-EtPh)₂DABMe₂] PdMe (MeCN) }BAF

[(2,6-EtPh)₂DABMe₂]PdMeCl (0.200 g, 0.396 mmol) was dissolved in 10 mL of acetonitrile to give an orange solution. To this was added NaBAF (0.350 g, 0.396 mmol). The reaction mixture turned bright yellow and NaCl precipitated. The reaction mixture was stirred at room temperature for 30 min and then filtered through a Celite® pad. The Celite® pad was extracted with 5 mL of acetonitrile. The combined filtrate and extract was concentrated in vacuo to afford an orange solid, recrystallization of which from methylene chloride / petroleum ether at -40°C afforded 0.403 g of the title compound as orange crystals (Yield = 74%). ¹H NMR (CDCl₃) δ 7.68 (s, 8H, H_{ortho} of anion), 7.51 (s, 4H, H_{para} of anion), 7.33-7.19 (mult, 6H, H_{aryl} of cation), 2.56-2.33 (mult, 8H, CH_2CH_3), 2.11 (s, 3H, N=CMe), 2.09 (s, 3H, N=CMe'), 1.71 (s, 3H, N=CMe),

1.27-1.22 (mult, 12H, CH_2CH_3), 0.41 (s, 3H, Pd-Me).

Example 51

{ [(2,6-EtPh)₂DABMe₂] PdMe (MeCN) }SbF₆

A procedure analogous to that used in Example 50, using AgSbF₆ in place of NaBAF, afforded the title compound as yellow crystals in 99% yield after recrystallization from methylene chloride/petroleum ether at -40°C.

Example 52

[(COD) PdMe(NCMe)] SbF₆

10 To (COD) PdMeCl (1.25 g, 4.70 mmol) was added a solution of acetonitrile (1.93 g, 47.0 mmol) in 20 mL methylene chloride. To this clear solution was added $AgSbF_6$ (1.62 g, 4.70 mmol). A white solid immediately precipitated. The reaction mixture was stirred at room temperature for 45 min, and then filtered. The yellow 15 filtrate was concentrated to dryness, affording a yellow solid. This was washed with ether and dried, affording 2.27 g of [(COD)PdMe(NCMe)]SbF6 as a light yellow powder (yield = 95%). ¹H NMR (CD₂Cl₂) δ 5.84 (mult, 2H, CH=CH), 5.42 (mult, 2H, CH'=CH'), 2.65 20 (mult, 4H, CHH'), 2.51 (mult, 4H, CHH'), 2.37 (s, 3H, NCMe), 1.18 (s, 3H, Pd-Me).

Example 53

[(COD) PdMe(NCMe)]BAF

A procedure analogous to that used in Example 52, using NaBAF in place of AgSbF₆, afforded the title compound as a light beige powder in 96% yield.

Example 54

{ [(2-t-BuPh)₂DABMe₂] PdMe (MeCN) } SbF₅

To a suspension of (2-t-BuPh)₂DABMe₂ (0.138 g, 0.395 mmol) in 10 mL of acetonitrile was added [(COD)PdMe(NCMe)]SbF₆ (0.200 g, 0.395 mmol). resulting yellow solution was stirred at room temperature for 5 min. It was then extracted with 3 x 10 mL of petroleum ether. The yellow acetonitrile phase was concentrated to dryness, affording a bright 10 yellow powder. Recrystallization from methylene chloride/petroleum ether at -40 °C afforded 180 mg of the title product as a bright yellow powder (yield = ¹H NMR (CD_2Cl_2) δ 7.57 (dd, 2H, H_{aryl}), 7.32 (mult, 4H, H_{aryl}), 6.88 (dd, 2H, H_{aryl}), 6.78 (dd, 2H, H_{arvl}), 2.28 (s, 3H, N=CMe), 2.22 (s, 3H, N=CMe'), 1.78 (s, 3H, N≡CMe), 1.48 (s, 18H, ^tBu), 0.52 (s, 3H, Pd-Me).

Example 55

{ [(Np)₂DABMe₂] PdMe (MeCN) }SbF₆

A procedure analogous to that used in Example 54, using $(\mathrm{Np})_2\mathrm{DABMe}_2$ in place of $(2\text{-t-BuPh})_2\mathrm{DABMe}_2$, afforded the title compound as an orange powder in 52% yield after two recrystallizations from methylene chloride/petroleum ether. ¹H NMR $(\mathrm{CD}_2\mathrm{Cl}_2)$ δ 8.20-7.19 (mult, 14 H, Haromatic), 2.36 (d, J = 4.3 Hz, 3H, N=CMe), 2.22 (d, J = 1.4 Hz, 3H, N=CMe'), 1.32 (s, 3H, NCMe), 0.22 (s, 3H, Pd-Me).

Example 56

{ [(Ph₂CH)₂DABH₂] PdMe (MeCN) }SbF₆

A procedure analogous to that used in Example 54, using $(Ph_2CH)_2DABH_2$ in place of $(2-t-BuPh)_2DABMe_2$, afforded the title compound as a yellow microcrystalline solid. ¹H NMR $(CDCl_3)$ δ 7.69 (s, 1H, N=CH), 7.65 (s, 1H, N=CH'), 7.44-7.08 (mult, 20H, Haryl), 6.35 (2, 2H, CHPh₂), 1.89 (s, 3H, NCMe), 0.78 (s, 3H, Pd-Me).

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Example 57

{ [(2-PhPh)₂DABMe₂] PdMe (MeCN) }SbF₆

A procedure analogous to that used in Example 54, using $(2-PhPh)_2DABMe_2$ in place of $(2-t-BuPh)_2DABMe_2$, afforded the title compound as a yellow-orange powder in 90% yield. Two isomers, due to cis or trans orientations of the two ortho phenyl groups on either side of the square plane, were observed by ¹H NMR. ¹H NMR (CD_2Cl_2) δ 7.80-6.82 (mult, 18H, H_{aryl}), 1.98, 1.96, 1.90, 1.83, 1.77, 1.73 (singlets, 9H, N=CMe, N=CMe', NCMe for cis and trans isomers), 0.63, 0.61 (singlets, 3H, Pd-Me for cis and trans isomers).

Example 58

{ [(Ph)₂DAB(cyclo-CMe₂CH₂CMe₂-)] PdMe(MeCN) }BAF To a solution of [(COD)PdMe(NCMe)]BAF (0.305 g, 15 0.269 mmol) dissolved in 15 mL of acetonitrile was added N, N'-diphenyl-2, 2', 4, 4'-tetramethylcyclopentyldiazine (0.082 g, 0.269 mmol). A gold colored solution formed rapidly and was stirred at room temperature for 20 min. The solution was then 20 extracted with 4 x 5 mL petroleum ether, and the acetonitrile phase concentrated to dryness to afford a yellow powder. This was recrystallized from methylene chloride/petroleum ether at -40°C to afford 0.323 g (90%) of the title compound as a yellow-orange, 25 crystalline solid. ^{1}H NMR (CDCl₃) δ 7.71 (s, 8H, H_{ortho} of anion), 7.54 (s, 4H, H_{para} of anion), 7.45-6.95 (mult, 10H, H_{aryl} of cation), 1.99 (s, 2H, CH_2), 1.73 (s, 3H, NCMe), 1.15 (s, 6H, Me₂), 1.09 (s, 6H, Me'₂),30 0.48 (s, 3H, Pd-Me).

Example 59

{[(2,6-i-PrPh)₂DABMe₂]Pd(CH₂CH₂CO₂Me)}SbF₆
Under a nitrogen atmosphere {[(2,6-i-PrPh)₂DABMe₂]PdMe(Et₂O)}SbF₆ (3.60 g, 4.30 mmol) was weighed into a round bottom flask containing a magnetic stirbar. To this was added a -40°C solution of methyl acrylate (1.85 g, 21.5 mmol) dissolved in 100 ml of methylene chloride. The resulting orange solution was

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temperature. The reaction mixture was then concentrated to dryness, affording a yellow-brown solid. The crude product was extracted with methylene chloride, and the orange-red extract concentrated, layered with an equal volume of petroleum ether, and cooled to -40°C. This afforded 1.92 g of the title compound as yellow-orange crystals. An additional 1.39 g was obtained as a second crop from the mother liquor; total yield = 91%. ¹H NMR (CD₂Cl₂) & 7.39-7.27 (mult, 6H, H_{aryl}), 3.02 (s, 3H, OMe), 2.97 (sept, 4H, CHMe₂), 2.40 (mult, 2H, CH₂), 2.24 (s, 3H, N=CMe), 2.22 (s, 3H, N=CMe'), 1.40-1.20 (mult, 26H, CHMe₂ and CH₂'), 0.64 (mult, 2H, CH₂'').

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Example 60

 $\{[(2,6-i-PrPh)_2DABH_2]Pd(CH_2CH_2CH_2CO_2Me)\}SbF_6$ AgSbF₆ (0.168 g, 0.489 mmol) was added to a -40° C solution of {[(2,6-i-PrPh)2DABH2]PdMeCl (0.260 g, 0.487 mmol) and methyl acrylate (0.210 g, 2.44 mmol) in 10 mL methylene chloride. The reaction mixture was stirred for 1 h while warming to room temperature, and then filtered. The filtrate was concentrated in vacuo to give a saturated solution of the title compound, which was then layered with an equal volume of petroleum ether and cooled to -40°C. Red-orange crystals precipitated from the solution. These were separated by filtration and dried, affording 0.271 g of the title compound (68% yield). ¹H NMR (CD₂Cl₂) δ 8.38 (s, 1H, N=CH), 8.31 (s, 1H, N=CH'), 7.41-7.24 (mult, 6H, Harv1), 3.16 (mult, 7H, OMe and CHMe2), 2.48 (mult, 2H, CH₂), 1.65 (t, 2H, CH₂'), 1.40-1.20 (mult, 24H, CHMe₂), 0.72 (mult, 2H, CH2'').

Example 61

 $\{[(2,6-i-$

 $\label{eq:prph} $$\Pr{\text{Ph}}_2$DABMe$_2$ $\Pr{\text{Ch}}_2$CH$_2$CO$_2$Me$_3$ $\{(2,6-i-\text{PrPh})_2$DABMe$_2$ $\Pr{\text{Ph}}_2$DABMe$_2$ $\Pr{\text{Ch}}_2$CO$_2$Me$_3$ $(0.038\ \text{g},\ 0.067\ \text{mmol})$$ and methyl acrylate (0.028\ \text{g},\ 0.33\ \text{mmol})$ were dissolved in CD_2Cl_2$. To this solution was added $B(C_6F_5)_3$ (0.036)$

g, 0.070 mmol). ¹H NMR of the resulting reaction mixture showed formation of the title compound.

Example 62

A 100 mL autoclave was charged with chloroform (50 mL), {[(2-t-BuPh)₂DABMe₂]PdMe(NCMe)}SbF₆- (0.090 g, 0.12 5 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at 25°C and 2.1 MPa ethylene for 3 h. ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.695 q of branched polyethylene. The number average molecular 10 weight (M_n) , calculated by ¹H NMR integration of aliphatic vs. olefinic resonances, was 1600. degree of polymerization, DP, was calculated on the basis of the 1H NMR spectrum to be 59; for a linear polymer this would result in 18 methyl-ended branches 15 per 1000 methylenes. However, based on the 1H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 154. Therefore, it may be concluded that this material was branched 20 polyethylene. ¹H NMR (CDCl₃) δ 5.38 (mult, vinyl H's), 1.95 (mult, allylic methylenes), 1.62 (mult, allylic methyls), 1.24 (mult, non-allylic methylenes and methines), 0.85 (mult, non-allylic methyls).

Example 63

A suspension of $\{[(2-t-BuPh)_2DABMe_2]PdMe(NCMe)\}SbF_6$ (0.015 g, 0.02 mmol) in 5 mL FC-75 was agitated under 2.8 MPa of ethylene for 30 min. The pressure was then increased to 4.1 MPa and maintained at this pressure for 3 h. During this time the reaction temperature varied between 25 and $40^{\circ}C$. A viscous oil was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. The number average molecular weight (M_n) , calculated by 1H NMR integration of aliphatic vs. olefinic resonances, was 2600. DP for this material was calculated on the basis of the 1H NMR spectrum to be 95; for a linear polymer this would result in 11 methyl-ended branches per 1000 methylenes. However, based on the 1H NMR

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spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 177.

Example 64

A 100 mL autoclave was charged with chloroform (55 mL), {[(2-PhPh)₂DABMe₂]PdMe(NCMe)}SbF₆ (0.094 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred at 25°C and 2.1 MPa ethylene for 3 h. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 2.27 g of a pale yellow oil. Mn was calculated on the basis of ¹H NMR integration of aliphatic vs. olefinic resonances to be 200. The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 7.2; for a linear polymer this would result in 200 methyl-ended branches per 1000 methylenes. However, based on the ¹H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 283.

Example 65

A suspension of [(2-PhPh)2DABMe2]PdMe(NCMe)}SbF6 20 (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (329 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried in vacuo. 25 Mn was calculated on the basis of ¹H NMR integration of aliphatic vs. olefinic resonances to be 700. The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 24.1; for a linear polymer this would result in 45 methyl-ended branches per 1000 methylenes. However, based on the 1H NMR spectrum the 30 number of methyl-ended branches per 1000 methylenes was calculated to be 173.

Example 66

A 100 mL autoclave was charged with FC-75 (50 mL), $\left\{ \text{(Ph}_2\text{DABMe}_2\text{)PdMe} \text{(NCMe)} \right\} \text{SbF}_6 \quad \text{(0.076 g, 0.12 mmol)} \text{ and }$ ethylene (2.1 MPa). The reaction mixture was stirred at 24°C for 1.5 h. The ethylene pressure was then vented, and the FC-75 mixture removed from the reactor.

mixture by decanting off the FC-75. The reactor was washed out with 2 x 50 mL CHCl₃, and the washings added to the oil. Volatiles removed from the resulting solution in vacuo to afford 144 mg of an oily solid. Mn was calculated on the basis of ¹H NMR integration of aliphatic vs. olefinic resonances to be 400. The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 13.8; for a linear polymer this would result in 83 methyl-ended branches per 1000 methylenes. However, based on the ¹H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 288.

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Example 67

- 15 A 100 mL autoclave was charged with chloroform (50 mL), {[(2,6-EtPh)₂DABMe₂]PdMe(NCMe)}BAF (0.165 g, 0.12 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred under 2.1 MPa of ethylene for 60 min; during this time the temperature inside the reactor 20 increased from 22 to 48°C. The ethylene pressure was then vented and volatiles removed from the reaction mixture in vacuo to afford 15.95 g of a viscous oil. ¹H NMR of this material showed it to be branched polyethylene with 135 methyl-ended branches per 1000 25 methylenes. GPC analysis in trichlorobenzene (vs. a linear polyethylene standard) gave $M_n = 10,400$, $M_w =$ 22,100.

Example 68

This was run identically to Example 67, but with {[(2,6-EtPh)₂DABMe₂]PdMe(NCMe)}SbF₆ (0.090 g, 0.12 mmol) in place of the corresponding BAF salt. The temperature of the reaction increased from 23 to 30°C during the course of the reaction. 5.25 g of a viscous oil was isolated, ¹H NMR of which showed it to be branched polyethylene with 119 methyl-ended branches per 1000 methylenes.

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Example 69

A suspension of $\{[(Np)_2DABMe_2]PdMe(NCMe)\}SbF_6$ (0.027~g,~0.02~mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h; during this time the temperature inside the reactor varied between 25 and $40^{\circ}C$. Two FC-75 insoluble fractions were isolated from the reaction mixture. One fraction, a non-viscous oil floating on top of the FC-75, was removed by pipette and shown by ^{1}H NMR to be branched ethylene oligomers for which M_n = 150 and with 504 methyl-ended branches per 1000 methylenes. The other fraction was a viscous oil isolated by removing FC-75 by pipette; it was shown by ^{1}H NMR to be polyethylene for which M_n = 650 and with 240 methyl-ended branches per 1000 methylenes.

Example 70

A suspension of {[(Ph₂CH)₂DABH₂]PdMe(NCMe)}SbF₆ (0.016 g, 0.02 mmol) in 5 mL FC-75 was agitated under 1.4 MPa of ethylene for 3 h 40 min. During this time the reaction temperature varied between 23 and 41°C. A viscous oil (43 mg) was isolated from the reaction mixture by decanting off the FC-75 and dried *in vacuo*. Mn was calculated on the basis of ¹H NMR integration of aliphatic vs. olefinic resonances to be approximately 2000. The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 73; for a linear polymer this would result in 14 methyl-ended branches per 1000 methylenes. However, based on the ¹H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 377.

Example 71

A 100 mL autoclave was charged with FC-75 (50 mL), $(\{Ph_2DAB(cyclo - CMe_2CH_2CMe_2-)\}PdMe(MeCN))BAF^-(0.160 g, 0.12 mmol)$ and ethylene (2.1 MPa). The reaction mixture was stirred at 24-25°C for 3.5 h. The ethylene pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 mixture was extracted with chloroform, and the chloroform extract concentrated to dryness affording 0.98 g of an oil. Mn

was calculated on the basis of ¹H NMR integration of aliphatic vs. olefinic resonances to be 500. The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 19.5; for a linear polymer this would result in 57 methyl-ended branches per 1000 methylenes. However, based on the ¹H NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 452.

Example 72

10 A 100 mL autoclave was charged with FC-75 (50 mL), $\{[(4-NMe_2Ph)_2DABMe_2]PdMe(MeCN)\}SbF_6$ (MeCN) (0.091 g, 0.12 mmol) and ethylene (2.1 MPa). The reaction mixture was stirred at 24°C for 1.5 h. pressure was then vented, and the cloudy FC-75 mixture removed from the reactor. The FC-75 was extracted with 15 3 x 25 mL of chloroform. The reactor was washed out with 3 x 40 mL CHCl3, and the washings added to the extracts. Volatiles removed from the resulting solution in vacuo to afford 556 mg of an oil. Mn was calculated on the basis of ¹H NMR integration of 20 aliphatic vs. olefinic resonances to be 200. degree of polymerization, DP, was calculated on the basis of the 1H NMR spectrum to be 8.4; for a linear polymer this would result in 154 methyl-ended branches per 1000 methylenes. However, based on the ¹H NMR 25 spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 261.

Example 73

Under nitrogen, a 250 mL Schlenk flask was charged with 10.0 g of the monomer $CH_2=CHCO_2CH_2(CF_2)_nCF_3$ (avg n = 9), 40 mL of methylene chloride, and a magnetic stirbar. To the rapidly stirred solution was added [(2,6-i-PrPh)₂DABMe₂]PdMe(OEt₂)}SbF₆ (0.075 g, 0.089 mmol) in small portions. The resulting yellow-orange solution was stirred under 1 atm of ethylene for 18 h. The reaction mixture was then concentrated, and the viscous product extracted with ~ 300 mL of petroleum ether. The yellow filtrate was concentrated to

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dryness, and extracted a second time with ~ 150 mL petroleum ether. ~ 500 mL of methanol was added to the filtrate; the copolymer precipitated as an oil which adhered to the sides of the flask, and was isolated by decanting off the petroleum ether/ methanol mixture. The copolymer was dried, affording 1.33 g of a slightly viscous oil. Upon standing for several hours, an additional 0.70 g of copolymer precipitated from the petroleum ether/ methanol mixturé. By 1H NMR 10 integration, it was determined that the acrylate content of this material was 4.2 mole%, and that it contained 26 ester and 87 methyl-ended branches per 1000 methylenes. GPC analysis in tetrahydrofuran (vs. a PMMA standard) gave $M_n = 30,400, M_w = 40,200.$ ¹H NMR. 15 (CDCl₃) δ 4.36 (t, CH₂CH₂CO2CH₂CH₂R_f), 2.45 (mult, $CH_2CH_2CO2CH_2CH_2R_f$), 2.31 (t, $CH_2CH_2CO2CH_2CH_2R_f$), 1.62 (mult, $CH_2CH_2CO2CH_2CH_2R_f$), 1.23 (mult, other methylenes and methines), 0.85 (mult, methyls). 13C NMR gave branching per 1000 CH2: Total methyls (91.3), Methyl 20 (32.8), Ethyl(20), Propyl (2.2), Butyl (7.7), Amyl (2.2), ≥Hex and end of chains (22.1). GPC analysis in THF gave Mn = 30,400, Mw = 40,200 vs. PMMA.

Example 74

A 100 mL autoclave was charged with 25 $[Pd(CH_3CH_2CN)_4](BF_4)_2$ (0.058 g, 0.12 mmol) and chloroform (40 mL). To this was added a solution of (2,6-i-PrPh) 2DABMe2 (0.070 g, 0.17 mmol) dissolved in 10 mL of chloroform under ethylene pressure (2.1 MPa). The pressure was maintained at 2.1 MPa for 1.5 h, 30 during which time the temperature inside the reactor increased from 22 to 35°C. The ethylene pressure was then vented and the reaction mixture removed from the reactor. The reactor was washed with 3 x 50 mL of chloroform, the washings added to the reaction mixture, and volatiles removed from the resulting solution in vacuo to afford 9.77 g of a viscous oil. 1H NMR of this material showed it to be branched polyethylene with 96 methyl-ended branches per 1000 methylenes.

Example 75

A 100 mL autoclave was charged with $[Pd(CH_3CN)_4](BF_4)_2$ (0.053 g, 0.12 mmol) and chloroform (50 mL). To this was added a solution of (2,6-i-PrPh)2DABMe2 (0.070 g, 0.17 mmol) dissolved in 10 mL of chloroform under ethylene pressure (2.1 MPa). pressure was maintained at 2.1 MPa for 3.0 h, during which time the temperature inside the reactor increased from 23 to 52°C. The ethylene pressure was then vented 10 and the reaction mixture removed from the reactor. reactor was washed with 3 x 50 mL of chloroform, the washings added to the reaction mixture, and volatiles removed from the resulting solution in vacuo to afford 25.98 g of a viscous oil. ¹H NMR of this material showed it to be branched polyethylene with 103 methyl-15 ended branches per 1000 methylenes. GPC analysis in trichlorobenzene gave $M_n = 10,800$, $M_w = 21,200$ vs. linear polyethylene.

Example 76

20 A mixture of 20 mg (0.034 mmol) of [(2,6-i-PrPh) DABH2] NiBr2 and 60 mL dry, deaerated toluene was magnetically-stirred under nitrogen in a 200-mL threenecked flask with a gas inlet tube, a thermometer, and a gas exit tube which vented through a mineral oil bubbler. To this mixture, 0.75 mL (65 eq) of 3M 25 poly(methylalumoxane) (PMAO) in toluene was added via The resulting deep blue-black catalyst solution was stirred as ethylene was bubbled through at about 5 ml and 1 atm for 2 hr. The temperature of the mixture rose to 60°C in the first 15 min and then 30 dropped to room temperature over the course of the reaction.

The product solution was worked up by blending with methanol; the resulting white polymer was washed with 2N HCl, water, and methanol to yield after drying (50°C/vacuum/nitrogen purge) 5.69g (6000 catalyst turnovers) of polyethylene which was easily-soluble in hot chlorobenzene. Differential scanning calorimetry

exhibited a broad melting point at 107°C (67 J/g). Get permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory):

5 M_n=22,300; M_w=102,000; M_w/M_n=4.56. ¹³C NMR analysis: branching per 1000 CH₂: total Methyls (60), Methyl (41), Ethyl (5.8), Propyl (2.5), Butyl (2.4), Amyl (1.2), ≥Hexyl and end of chain (5); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and could be stretched and drawn without elastic recovery.

Example 77

In a Parr® 600-mL stirred autoclave under nitrogen was combined 23 mg (0.039 mmol) of [(2,6-i-15 PrPh)DABH2]NiBr2, 60 mL of dry toluene, and 0.75 mL of poly(methylalumoxane) at 28°C. The mixture was stirred, flushed with ethylene, and pressurized to 414 kPa with ethylene. The reaction was stirred at 414 kPa for 1 hr; the internal temperature rose to 31°C over 20 this time. After 1 hr, the ethylene was vented and 200 mL of methanol was added with stirring to the autoclave. The resulting polymer slurry was filtered; the polymer adhering to the autoclave walls and impeller was scraped off and added to the filtered 25 polymer. The product was washed with methanol and acetone and dried (80°C/vacuum/nitrogen purge) to yield 5.10g (4700 catalyst turnovers) of polyethylene. Differential scanning calorimetry exhibited a melting 30 point at 127°C (170 J/g). Gel permeation chromatography (trichlorobenzene, 135°C; polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=49,300$; $M_w=123,000$; $M_w/M_{n}=2.51$. Intrinsic viscosity (trichlorobenzene, 135°C): 1.925 dL/q. Absolute molecular weight averages 35 corrected for branching: $M_n=47,400$; $M_w=134,000$; $M_w/M_n=2.83$. 13C NMR analysis; branching per 1000 CH₂: total Methyls (10.5), Methyl (8.4), Ethyl (0.9), Propyl

(0), Butyl (0), ≥Butyl and end of chain (1.1); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). A film of polymer (pressed at 200°C) was strong and stiff and could be stretched and drawn without elastic recovery. This polyethylene is much more crystalline and linear than the polymer of Example 76. This example shows that only a modest pressure increase from 1 atm to 414 kPa allows propagation to successfully compete with rearrangement and isomerization of the polymer chain by this catalyst, thus giving a less-branched, morecrystalline polyethylene.

Example 78

A mixture of 12 mg (0.020 mmol) of [(2,6-i-15 PrPh) DABH2] NiBr2 and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 15°C in a 100-mL three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL 20 of poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was stirred for 5 min and allowed to warm to room temperature. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 15 25 mL (about 10g) of cis-2-butene. The catalyst solution was stirred as the cis-2-butene was added as a liquid all at once, and the mixture was stirred for 16 hr. The product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary 30 evaporation yielded 0.35g (300 catalyst turnovers) of a light yellow grease, poly-2-butene. 13C NMR analysis; branching per 1000 CH2: total Methyls (365), Methyl (285), Ethyl (72), ≥Butyl and end of chain (8); chemical shifts were referenced to the solvent 35 chloroform-d₁ (77 ppm).

Listed below are the ¹³C NMR data upon which the above analysis is based.

13_C NMR Dáta

	CDCl ₃ , RT,	0 0'5M Cr	ACAC		
Freq ppm	Intensity	0.03 Ci	anone.		
41.6071	11.2954				
41.1471	13.7193			٠,	
38.6816	3.55568				
37.1805	7.07882				
36.8657	33.8859				
36.7366	35.1101				
36.6196	33.8905				
36.2645	12.1006				
35.9094	13.3271				
35.8004	11.8845				
35.5785	4.20104				
34.7351	24.9682				
34.4325	39.3436				
34.3114	59.2878				
34.1177	125.698 121.887				
33.9886					
33.8837	120.233				
33.5326 33.004	49.8058				
-	132.842				
32.7377	51.2221				
32.657	55.6128				
32.3705	18.1589				
	9.27643				
31.3818	16.409				
31.0066	15.1861				
30.0946	41.098				
29.9736	42.8009		•		
29.7072	106.314				
29.3602	60.0884				
29.2512	35.0694				
29.114	26.6437				
28.9769	29.1226				
27.9358	3.57351				
27.7501	3.56527				
27.0682	14.6121				
26.7333	81.0769		•		
26.3257	14.4591				
26.015	11.8399				*
25.3008	8.17451				
25.0627	5.98833				
22.4801	3.60955		2B4		
22.3308	10.4951		2B ₅ +,	EOC	
19.6192	90.3272		1B ₁		
19.4618	154.354		1B ₁		
19.3085	102.085		1B ₁		
18.9937	34.7667		1B ₁		
18.8525	38.7651		1B ₁		
13.7721	11.2148	•	1B ₄ +,	EOC,	1E3
11.0484	54.8771		1B ₂		
10.4552	10.8437	•	1B ₂		
10.1283	11.0735		1B ₂		
9.99921	9.36226		1B ₂		

Example 79

A mixture of 10 mg (0.017 mmol) of [(2,6-i-PrPh) DABH2] NiBr2 and 40 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL 5 three-necked flask with an addition funnel, a thermometer, and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.5 mL of 3M poly(methylalumoxane) in toluene was added via syringe; the resulting burgundy catalyst solution was 10 stirred at 5°C for 40 min. Into the addition funnel was condensed (via a Dry Ice condenser on the top of the funnel) 20 mL (about 15 g) of 1-butene. catalyst solution was stirred as the 1-butene was added as a liquid all at once. The reaction temperature rose 15 to 50°C over 30 min and then dropped to room temperature as the mixture was stirred for 4 hr. product solution was treated with 1 mL of methanol and was filtered through diatomaceous earth; rotary evaporation yielded 6.17 g (1640 catalyst turnovers) of 20 clear, tacky poly-1-butene rubber. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=64,700$; $M_w=115,000$; $M_w/M_{\rm n}=1.77$. ¹³C NMR analysis; branching per 1000 CH₂: 25 total Methyls (399), Methyl (86), Ethyl (272), ≥Butyl and end of chain (41); chemical shifts were referenced to the solvent chloroform- d_1 (77 ppm). This example demonstrates the polymerization of an alpha-olefin and shows the differences in branching between a polymer 30 derived from a 1-olefin (this example) and a polymer derived from a 2-olefin (Example 78). This difference shows that the internal olefin of Example 78 is not first isomerized to an alpha-olefin before polymerizing; thus this catalyst is truly able to 35 polymerize internal olefins.

Listed below are the ^{13}C NMR data upon which the above analysis is based.

¹³C NMR Data

	CDC13, RT, 0.05	M CrA	CAC	
Freq ppm	Intensity			
43.8708	6.42901			
41.5304	11.1597			
41.0825	16.1036			
38.7623	103.647			
38.1247	50.3288			
37.3338	24.6017			
36.8173	30.0925			
35.756	55.378			
35.0337	22.3563			
34.1419	64.8431		,	
33.8514	55.3508			
33.4116	90.2438			
33.0645	154.939			
32.7094	51.3245			
32.431	23.0013	3B ₅		
30.946	12.8866	3B ₆ +		
30.1551	26.1216			
29.7516	54.6262			
29.4248	40.7879			
27.6008	8.64277			
27.2417	20.1564			
27.1207	21.9735			
26.7777	45.0824			
26.0755	66.0697			
25.6599	77.1097			
24.3807	8.9175			
23.4809	32.0249	2B ₄ ,	2B ₅ +,	2EOC
22.8393	8.06774			
22.1372	16.4732			
19.4981	57.7003	1B ₁		
19.3609	70.588	1B ₁		
15.132	17.2402	1B ₄ +		
13.8448	7.9343	1B ₄ +		
12.2509	27.8653		•	
12.037	27.0118			
11.0766	6.61931	1B ₂		
10.2938	98.0101	1B ₂		
10.1364	104.811	1B ₂		•

Example 80

A 22-mg (0.037-mmol) sample of [(2,6-i-PrPh)DABH2]NiBr2 was introduced into a 600-mL stirred Parr® autoclave under nitrogen. The autoclave was sealed and 75 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe through a port on the autoclave head. Then 0.6 mL of 3M poly(methylalumoxane) was added via syringe and stirring was begun. The autoclave was pressurized with

ropylene to 414 kPa and stirred with continuous propylene feed. There was no external cooling. internal temperature quickly rose to 33°C upon initial propylene addition but gradually dropped back to 24°C over the course of the polymerization. After about 7 min, the propylene feed was shut off and stirring was continued; over a total polymerization time of 1.1 hr, the pressure dropped from 448 kPa to 358 kPa. propylene was vented and the product, a thin, honey-10 colored solution, was rotary evaporated to yield 1.65q of a very thick, brown semi-solid. This was dissolved in chloroform and filtered through diatomaceous earth; concentration yielded 1.3 g (835 catalyst turnovers) of tacky, yellow polypropylene rubber. Gel permeation 15 chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory): $M_n=7,940$; $M_w=93,500$; $M_{\rm w}/M_{\rm p}=11.78$.

Example 81

20 A mixture of 34 mg (0.057 mmol) of [(2,6-i-PrPh) DABH2] NiBr2 and 20 mL dry, deaerated toluene was magnetically-stirred under nitrogen at 5°C in a 100-mL three-necked flask with a thermometer and a nitrogen inlet tube which vented through a mineral oil bubbler. To this mixture, 0.7 mL of 3M poly(methylalumoxane) in toluene was added via syringe and the resulting deep blue-black solution was stirred for 30 min at 5°C. this catalyst solution was added 35 mL of dry, deaerated cyclopentene, and the mixture was stirred and 30 allowed to warm to room temperature over 23 hr. blue-black mixture was filtered through alumina to remove dark blue-green solids (oxidized aluminum compounds from PMAO); the filtrate was rotary evaporated to yield 1.2 g (310 catalyst turnovers) of clear liquid cyclopentene oligomers. 35

Example 82

A 20-mg (0.032 mmol) sample of [(2,6-i-PrPh)DABMe2]NiBr2 was placed in Parr® 600-mL stirred

autoclave under nitrogen. The autoclave was sealed and 100 mL of dry, deaerated toluene and 0.6 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port, and mixture was stirred under nitrogen at 20°C for 50 min. The autoclave body was immersed in a flowing water bath and the autoclave was then pressurized with ethylene to 2.8 MPa with stirring as the internal temperature rose to 53°C. The autoclave was stirred at 2.8 MPa (continuous ethylene feed) for 10 min as the temperature dropped to 29°C, and the ethylene was then vented. The mixture stood at 1 atm for 10 min; vacuum was applied to the autoclave for a few minutes and then the autoclave was opened.

The product was a stiff, swollen polymer mass 15 which was scraped out, cut. up, and fed in portions to 500 mL methanol in a blender. The polymer was then boiled with a mixture of methanol (200 mL) and trifluoroacetic acid (10 mL), and finally dried under high vacuum overnight to yield 16.8g (18,700 catalyst 20 turnovers) of polyethylene. The polymer was somewhat heterogeneous with respect to crystallinity, as can be seen from the differential scanning calorimetry data below; amorphous and crystalline pieces of polymer could be picked out of the product. Crystalline 25 polyethylene was found in the interior of the polymer mass; amorphous polyethylene was on the outside. crystalline polyethylene was formed initially when the ethylene had good access to the catalyst; as the polymer formed limited mass transfer, the catalyst 30 became ethylene-starved and began to make amorphous polymer. Differential scanning calorimetry: (crystalline piece of polymer): mp: 130°C (150J/g); (amorphous piece of polymer): -48°C (Tg); mp: 42°C (3J/g), 96°C (11J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_D=163,000$; $M_w=534,000$; $M_{\rm w}/M_{\rm r}=3.27$. This example demonstrates the effect of

ethylene mass transfer on the polymerization and shows that the same catalyst can make both amorphous and crystalline polyethylene. The bulk of the polymer was crystalline: a film pressed at 200°C was tough and stiff.

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Example 83

A 29-mg (0.047 mmol) sample of [(2,6-i-PrPh) DABMe2] NiBr2 was placed in Parr® 600-mL stirred. autoclave under nitrogen. The autoclave was sealed and 10 100 mL of dry, deaerated toluene and 0.85 mL of 3M poly(methylalumoxane) were injected into the autoclave through the head port. The mixture was stirred under nitrogen at 23°C for 30 min. The autoclave body was immersed in a flowing water bath and the autoclave was 15 pressurized with ethylene to 620 kPa with stirring. The internal temperature peaked at 38°C within 2 min. The autoclave was stirred at 620 kPa (continuous ethylene feed) for 5 min as the temperature dropped to The ethylene was then vented, the regulator was readjusted, and the autoclave was pressurized to 34.5 kPa (gauge) and stirred for 20 min (continuous ethylene feed) as the internal temperature dropped to 22°C. the middle of this 20 min period, the ethylene feed was temporarily shut off for 1 min, during which time the 25 autoclave pressure dropped from 34.5 kPa (gauge) to 13.8 kPa; the pressure was then restored to 34.5 kPa. After stirring 20 min at 34.5 kPa, the autoclave was once again pressurized to 620 kPa for 5 min; the internal temperature rose from 22°C to 34°C. The 30 ethylene feed was shut off for about 30 sec before venting; the autoclave pressure dropped to about 586 kPa.

The ethylene was vented; the product was a dark, thick liquid. Methanol (200 mL) was added to the autoclave and the mixture was stirred for 2 hr. The polymer, swollen with toluene, had balled up on the stirrer, and the walls and bottom of the autoclave were coated with white, fibrous rubbery polymer. The

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polymer was scraped out, cut up, and blended with methanol in a blender and then stirred with fresh boiling methanol for 1 hr. The white rubber was dried under high vacuum for 3 days to yield 9.6 g (7270 catalyst turnovers) of rubbery polyethylene. ¹H NMR analysis (CDCl₃): 95 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry: -51°C (Tg); mp: $39.5^{\circ}C$ (4J/g); mp: $76.4^{\circ}C$ (7J/g). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=223,000$; $M_w=487,000$; $M_w/M_n=2.19$.

The polyethylene of Example 83 could be cast from 15 hot chlorobenzene or pressed at 200°C to give a strong, stretchy, hazy, transparent film with good recovery. It was not easily chloroform-soluble. This example demonstrates the use of the catalyst's ability (see Example 82) to make both amorphous and crystalline 20 polymer, and to make both types of polymer within the same polymer chain due to the catalyst's low propensity to chain transfer. With crystalline blocks (due to higher ethylene pressure) on both ends and an amorphous region (due to lower- pressure, mass transfer-limited 25 polymerization) in the center of each chain, this polymer is a thermoplastic elastomer.

Example 84

A Schlenk flask containing 147 mg (0.100 mmol) of {[(2,6-i-PrPh)DABMe2]PdMe(OEt2)}BAF was cooled to -78°C, evacuated, and placed under an ethylene atmosphere. Methylene chloride (100 ml) was added to the flask and the solution was then allowed to warm to room temperature and stirred. The reaction vessel was warm during the first several hours of mixing and the solution became viscous. After being stirred for 17.4 h, the reaction mixture was added to ~600 mL of MeOH in order to precipitate the polymer. Next, the MeOH was decanted off of the sticky polymer, which was then

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dissolved in ~600 mL of petroleum ether. After being filtered through plugs of neutral alumina and silica gel, the solution appeared clear and almost colorless. The solvent was then removed and the viscous oil (45.31 g) was dried in vacuo for several days: 1 H NMR (CDCl₃, 400 MHz) δ 1.24 (CH₂, CH), 0.82 (m, CH₃); Branching: ~128 CH₃ per 1000 CH₂; DSC: $T_g = -67.7^{\circ}$ C. GPC: Mn = 29,000; Mw = 112,000.

Example 85

Following the procedure of Example 84 {[(2,6-i-PrPh)DABMe2]PdMe(OEt2)}BAF (164 mg, 0.112 mmol) catalyzed the polymerization of ethylene for 24 h in 50 mL of CH_2Cl_2 to give 30.16 g of polymer as a viscous oil. 1H NMR (C_6D_6) δ 1.41 (CH_2 , CH), 0.94 (CH_3); Branching: ~115 CH_3 per 1000 CH_2 ; GPC Analysis (THF, PMMA standards, RI Detector): M_w = 262,000; M_n = 121,000; PDI = 2.2; DSC: T_q = -66.8°C.

Example 86

The procedure of Example 84 was followed using 144 mg (0.100 mmol) of $\{[(2,6-i-PrPh)DABH_2]PdMe(OEt_2)\}BAF$ in 50 mL of CH_2Cl_2 and a 24 h reaction time. Polymer (9.68 g) was obtained as a free-flowing oil. ¹H NMR (CDCl₃, 400 MHz) δ 5.36 (m, RHC=CHR'), 5.08 (br s, RR'C=CHR''), 4.67 (br s, $H_2C=CRR'$), 1.98 (m, allylic H), 1.26 (CH₂, CH), 0.83 (m, CH₃); Branching: ~149 CH₃ per 1000 CH₂; DSC: $T_g = -84.6$ °C.

Example 87

A 30-mg (0.042-mmol) sample of [(2,6-i-PrPh)DABAn]NiBr₂ was placed in Parr® 600-mL stirred autoclave under nitrogen. The autoclave was sealed and 150 mL of dry toluene and 0.6 mL of 3M polymethylalumoxane were injected into the autoclave through the head port. The autoclave body was immersed in a flowing water bath and the mixture was stirred under nitrogen at 20°C for 1 hr. The autoclave was then pressurized with ethylene to 1.31 MPa with stirring for 5 min as the internal temperature peaked at 30°C. The ethylene was then vented to 41.4 kPa

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(gauge) and the mixture was stirred and fed ethylene at 41.4 kPa for 1.5 hr as the internal temperature dropped to 19°C. At the end of this time, the autoclave was again pressurized to 1.34 MPa and stirred for 7 min as the internal temperature rose to 35°C.

The ethylene was vented and the autoclave was briefly evacuated; the product was a stiff, solventswollen gel. The polymer was cut up, blended with 500 mL methanol in a blender, and then stirred overnight 10 with 500 mL methanol containing 10 mL of 6N HCl. stirred suspension in methanol/HCl was then boiled for 4 hr, filtered, and dried under high vacuum overnight to yield 26.1 g (22,300 catalyst turnovers) of polyethylene. Differential scanning calorimetry: -49°C 15 (Tg); mp: 116°C (42J/g). The melting transition was very broad and appeared to begin around room temperature. Although the melting point temperature is higher in this Example than in Example 76, the area under the melting endotherm is less in this example, 20 implying that the polymer of this Example is less crystalline overall, but the crystallites that do exist are more ordered. This indicates that the desired block structure was obtained. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene 25 reference, results calculated as polyethylene using universal calibration theory): $M_D=123,000$; $M_w=601,000$; $M_w/M_p=4.87$. The polyethylene of this example could be pressed at 200°C to give a strong, tough, stretchy, hazy film with partial elastic recovery. When the 30 stretched film was plunged into boiling water, it completely relaxed to its original dimensions.

Example 88

A 6.7-mg (0.011-mmol) sample of [(2,6-i-PrPh)DABMe₂]NiBr₂ was magnetically-stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene as 0.3 mL of 3M poly(methylalumoxane) was injected via syringe. The mixture was stirred at 23°C for 40 min to give a deep blue-green solution of

_atalyst. Dry, deaerated cyclopentene (10 mL) was injected and the mixture was stirred for 5 min. flask was then pressurized with ethylene at 20.7 MPa and stirred for 22 hr. The resulting viscous solution was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl. The methanol was decanted off and replaced with fresh methanol, and the polymer was stirred in boiling methanol for 3 hr. stretchy rubber was pressed between paper towels and dried under vacuum to yield 1.0g of 10 poly[ethylene/cyclopentene]. By 1H NMR analysis(CDCl3): 100 methyl carbons per 1000 methylene carbons. Comparison of the peaks attributable to cyclopentene (0.65 ppm and 1.75 ppm) with the standard polyethylene peaks (0.9 ppm and 1.3 ppm) indicates about a 10 mol% cyclopentene incorporation. polymer yield and composition represent about 2900 catalyst turnovers. Differential scanning calorimetry: -44°C (Tg). Gel permeation chromatography 20 (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=122,000$; $M_w=241,000$; $M_{w}/M_{n}=1.97$.

Listed below are the $^{13}\mathrm{C}$ NMR data upon which the 25 above analysis is based.

13C NMR data
TCB, 120C, 0.05M CrAcAc

Freq ppm 50.9168	Intensity 5.96663	
46.3865	3.27366	1 cme and/or 1,3 ccmcc
40.7527	40.5963	2 eme
40.567	41.9953	1,3 eme
40.3336	45.8477	1,3 eme
37.1985	60.1003	•
36.6998	41.2041	
36.0579	11.2879	
35.607	25.169	
34.4771	19.0834	
34.0845	22.8886	•
33.1243	20.1138	
32.8962	27.6778	
31.8406	75.2391	
30.0263	76.2755	

•		
29.6921	170.41	
28.9494	18.8754	
28.647	25.8032	
27.4588	22.2397	
27.1086	48.0806	
24.3236	3.31441	
22.5783	4.64411	2B ₅ +, 2 EOC
19.6712	43.1867	1B ₁
17.5546	1.41279	end group
14.3399	1.74854	1B ₃
13.8518	5.88699	1B ₄ +, 1EOC
10.9182	2.17785	2B ₁

Example 89

A 7.5-mg (0.013-mmol) sample of [(2,6-t-BuPh) DABMe2] NiBr2 was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 40 mL of dry, deaerated toluene as 0.5 mL of 3M poly(methylalumoxane). was injected via syringe. The mixture was stirred at 23°C for 1 hr to give a deep blue-green solution of catalyst. The flask was pressurized with ethylene at 10 20.7 kPa (gauge) and stirred for 20 hr. The solution, which had become a reddish-brown suspension, was poured into a stirred mixture of 200 mL methanol and 10 mL 6N HCl and was stirred at reflux for 1 hr. The methanol was decanted off and replaced with fresh methanol, and the white polymer was stirred in boiling methanol for 1 15 The stiff, stretchy rubber was pressed between paper towels and then dried under vacuum to yield 1.25 g (3380 catalyst turnovers) of polyethylene. 1H-1 NMR analysis (C6D6): 63 methyl carbons per 1000 methylene 20 carbons. Differential scanning calorimetry: -34°C (Tg); mp: 44°C (31J/g); mp: 101°C (23J/g).

Example 90

A 5.5 mg (0.0066 mmol) sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}SbF_6$ was allowed to stand at room temperature in air for 24 hr. A 100-mL three-neck flask with a magnetic stirrer and a gas inlet dip tube was charged with 40 mL of reagent methylene chloride and ethylene gas was bubbled through with stirring to saturate the solvent with ethylene. The sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}SbF_6$ was then rinsed

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into the flask with 5 mL of methylene chloride and ethylene was bubbled through with stirring for 5 hr. The clear yellow solution was rotary evaporated to yield 0.20 g (1080 catalyst turnovers) of a thick yellow liquid polyethylene.

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Example 91

A 600-mL stirred Parr® autoclave was sealed and flushed with nitrogen, and 100 mL of dry, deaerated toluene was introduced into the autoclave via gas tight syringe through a port on the autoclave head. The autoclave was purged with propylene gas to saturate the solvent with propylene. Then 45 mg (0.054 mmol) of {[(2,6-i-PrPh)2DABMe2]PdMe(Et2O)}SbF6 was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 45 mg of {[(2,6-i-PrPh)2DABMe2]PdMe (Et2O)}SbF6 under nitrogen in a glove box; then 1-2 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave was pressurized with propylene to 414 MPa and stirred for 2.5 hr, starting with continuous propylene feed. The autoclave was cooled in a running tap water bath at 22°C. The internal temperature quickly rose to 30°C upon initial propylene addition but soon dropped back to 22°C. After 0.5 hr, the propylene feed was shut off and stirring was continued. Over 2 hr, the pressure dropped from 41.4 MPa to 38.6 MPa. The propylene was then vented. product was a thin, honey-colored solution. Rotary evaporation yielded 2.3 g (1010 catalyst turnovers) of very thick, dark-brown liquid polypropylene which was almost elastomeric when cool. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polypropylene using universal calibration theory): $M_n=8,300$; $M_w=15,300$; $M_w/M_{n}=1.84$. ¹³C NMR analysis; branching per 1000 CH₂:

total Methyls (545), Propyl (1.3), ≥Butyl and end of chain (9.2); chemical shifts. The polymer exhibited a glass transition temperature of -44°C by differential scanning calorimetry.

5 Listed below are the ¹³C NMR data upon which the above analysis is based.

¹³C NMR data

		CDCl ₃ , RT, 0	.05M CrAcAc
	Freq ppm	Intensity	
	46.4978	13.2699	Methylenes
	45.8683	11.9947	Methylenes
	45.3639	10.959	Methylenes
	45.1783	11.3339	Methylenes
	44.5568	8.41708	Methylenes
	44.4398	7.69019	Methylenes
	44.3026	6.29108	Methylenes
	44.1372	6.73541	Methylenes
	43.5036	5.49837	Methylenes
	42.4262	5.03113	Methylenes
	41.6918	3.72552	Methylenes
	39.1537	4.23147	Methines and Methylenes
	38.7179	25.2596	Methines and Methylenes
	37.8664	10.0979	Methines and Methylenes
	37.6727	14.3755	Methines and Methylenes
	37.0755	17.623	Methines and Methylenes
	36.781	42.0719	Methines and Methylenes
	36.559	10.0773	Methines and Methylenes
	34.5495	5.34388	Methines and Methylenes
	34.3195	7.48969	Methines and Methylenes
	33.5488	12.6148	Methines and Methylenes
	33.351	20.5271	Methines and Methylenes
	32.7982	4.10612	Methines and Methylenes
	32.4108	22.781	Methines and Methylenes
	31.8701	5.90488	Methines and Methylenes
	31.5957	10.6988	Methines and Methylenes
	29.8364	44.4935	Methines and Methylenes
•	29.7072	103.844	Methines and Methylenes
	29.3925	152.645	Methines and Methylenes
	29.0293	6.71341	Methines and Methylenes
	27.6089	38.7993	Methines and Methylenes
	27.4193	10.3543	Methines and Methylenes
	27.0763	66.8261	Methines and Methylenes
	26.9552	92.859	Methines and Methylenes
	26.7615	55.7233	Methines and Methylenes
	26.3661	20.1674	Methines and Methylenes
	24.8529	16.9056	Methine Carbon of XXVIII
	23.1217	12.5439	Methine carbons of XXVIII and
			XXIX, 2B ₄ +, EOC
	22.6779	13.0147	Methine carbons of XXVIII and
			XXIX, 2B ₄ +, EOC
	22.5245	9.16236	Methine carbons of XXVIII and
			XXIX, 2B ₄ +, EOC
			-

22.3389	77.3342	Methine carbons of XXVIII and XXIX, 2B ₄ +, EOC
21.9757	9.85242	Methine carbons of XXVIII and XXIX, 2B ₄ +, EOC
21.1405	10.0445	Methyls
20.4182	8.49663	Methyls
19.9743	25.8085	Methyls
19.825	31.4787	Methyls
19.3811	44.9986	Methyls
19.1995	31.3058	Methyls
13.8569	6.37761	Methyls
13.8004	7.67242	Methyls
137.452	22.0529	Methyls
128.675	44.6993	Methyls
127.88	43.8939	Methyls
124.959	22.4025	Methyls
122.989	3.3312	Methyls

Example 92

A 600-mL stirred Parr® autoclave was sealed, flushed with nitrogen, and heated to 60°C in a water bath. Fifty mL (48 g; 0.56 mol) of dry, deaerated methyl acrylate was introduced into the autoclave via gas tight syringe through a port on the autoclave head and ethylene gas was passed through the autoclave at a low rate to saturate the solvent with ethylene before catalyst addition. Then 60 mg (0.07 mmol) of $\{[(2,6-i-$ PrPh) 2DABMe2] PdMe (Et20) }SbF6 was introduced into the autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 60 mg of { [(2,6-i-PrPh) 2DABMe2] PdMe(Et20) } SbF6 under nitrogen in a glove box; then 1 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head port. This method avoids having the catalyst in solution with no stabilizing ligands.

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The autoclave was pressurized with ethylene to 689

kPa and continuously fed ethylene with stirring for 4.5

hr; the internal temperature was very steady at 60°C.

The ethylene was vented and the product, a clear yellow solution, was rinsed out of the autoclave with chloroform, rotary evaporated, and held under high vacuum overnight to yield 1.56 g of thin light-brown liquid ethylene/methyl acrylate copolymer. The

infrared spectrum of the product exhibited a strong ester carbonyl stretch at 1740 cm $^{-1}$. 1 H-1 NMR analysis (CDC13): 61 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy 5 (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 16.6 mol% (37.9 wt%). This product yield and composition represent 480 ethylene turnovers and 96 methyl acrylate turnovers. 13C NMR analysis; 10 branching per 1000 CH2: total methyls (48.3), Methyl (20.8), Ethyl (10.5), Propyl (1), Butyl (8), ≥Amyl and End of Chain (18.1), methyl acrylate (94.4); esterbearing -CH(CH₂)_nCO₂CH₃ branches as a % of total ester: $n \ge 5$ (35.9), n = 4 (14.3), n = 1, 2, 3 (29.5), n = 0 (20.3); 15 chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results 20 calculated as polymethylmethacrylate using universal calibration theory): $M_n=3,370$; $M_w=5,450$; $M_w/M_n=1.62$. Listed below are the 13C NMR data upon which the above analysis is based.

13_{C NMR data}
TCB 120C, 0.05M CrAcAc

	TCB 1200	C, 0.05M Cracac
Freq ppm	Intensity	
53.7443	2.19635	CH ₂ Cl ₂ solvent impurity
50.9115	8.84408	
50.641	132.93	
45.5165	7.55996	MEB _O 43.8 ppm:2 adjacent MEB _O
39.6917	2.71676	120 1010 pp a a jacono 1120
39.2886	7.91933	
38.1639	13.843	
37.7926	26.6353	
37.1666	20.6759	• •
	•	•
36.6733	8.65855 17.6899	
34.6256		
34.4612	16.7388	·
34.1429	85.624	. ==
33.9095	124.997	1EB ₄ +
33.676	40.0271	Contributions from EB
33.2888	11.4719	Contributions from EB
32.8644	14.4963	Contributions from EB
32.3498	17.5883	Contributions from EB
32.0475	9.83096	Contributions from EB
31.8459	30.9676	Contributions from EB
31.7079	12.7737	Contributions from EB
31.5912	13.8792	Contributions from EB
31.0873	19.6266	Contributions from EB
30.6258	10.5512	
30.1324	58.6101	•
29.6497	169.398	
29.4322	48.5318	
29.1934	95.4948	
27.8619	8.70181	
27.4269	32.9529	
26.9283	78.0563	
26.5145	27.0608	
26.3554	14.0683	
25.4588	21.9081	2EB ₄ (tent)
25.3315	9.04646	2EB ₄ (tent)
24.9761	64.2333	2EB ₅ +
24.2069	10.771	BBB (beta-beta-B)
23.0451	9.50073	2B ₄
22.9337	6.90528	2B ₄
22.5518	30.0427	2B ₅ +, EOC
19.9842	1.87415	2B ₃
19.6288	17.125	1B ₁
19.1673	6.0427	1B ₁ '
16.7695	2.23642	
14.3	-	1B ₃
13.7882	34.0749	1B ₄ +, EOC
11.0774	4.50599	1B ₂
10.8705	10.8817	1B ₂
189.989	1.04646	EB ₀ Carbonyl
175.687	3.33867	EB ₀ Carbonyl
175.406	14.4124	EB ₀ Carbonyl
175.22	5.43832	EB ₀ Carbonyl
175.061	3.53125 ·	EB _O Carbonyl
		193
		- -

172.859	11.2356	EB ₁ + Carbonyl
172.605	102.342	EB ₁ + Carbonyl
172.09	7,83303	EB ₁ + Carbonyl
170.944	3.294	EB ₁ + Carbonyl

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Example 93

A 45-mg (0.048-mmol) sample of $\{(2,6-i-$ PrPh) 2DABAn] PdMe (Et 20) }SbF6 was placed in a 600-mL Parr ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methylene chloride, and the autoclave was pressurized to 414 kPa with ethylene. Ethylene was continuously fed at 414 kPa with stirring at 23-25°C for 3 hr; then the feed was shut off and the reaction was stirred for 12 hr more. At the end of this time, the autoclave was under 89.6 kPa (absolute). The autoclave was repressurized to 345 kPa with ethylene and stirred for 2 hr more as the pressure dropped to 255 kPa, showing that the catalyst was still active; the ethylene was then vented. The brown solution in the autoclave was rotary evaporated, taken up in chloroform, filtered through alumina to remove catalyst, and rotary evaporated and then held under high vacuum to yield 7.35 g of thick, yellow liquid polyethylene. ¹H NMR analysis (CDCl₃): 131 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M_n=10,300; M_w=18,100; $M_{W}/M_{D}=1.76$.

Example 94

A 79-mg (0.085-mmol) sample of {[(2,6-i-PrPh)2DABAn]PdMe(Et2O)}SbF6 was placed in a 600-mL Parr ® stirred autoclave under nitrogen. To this was added 50 mL of dry, deaerated methyl acrylate, and the autoclave was pressurized to 689 kPa with ethylene. The autoclave was warmed to 50°C and the reaction was stirred at 689 kPa for 70 hr; the ethylene was then vented. The clear yellow solution in the autoclave was filtered through alumina to remove catalyst, rotary

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evaporated, and held under high vacuum to yield 5.27 g of liquid ethylene/methyl acrylate copolymer. The infrared spectrum of the product exhibited a strong ester carbonyl stretch at 1740cm⁻¹. ¹H NMR analysis (CDCl₃): 70 methyl carbons per 1000 methylene carbons; 13.5 mol% (32 wt%) methyl acrylate. This yield and composition represent 12 methyl acrylate turnovers and 75 ethylene turnovers.

Example 95

10 A 67-mg (0.089-mmol) of $\{[(2,4,6-$ MePh) 2DABMe2] PdMe(Et2O) } SbF6 was placed in a 200-mL glass centrifuge bottle with a magnetic stir bar under To this was added 40 mL of dry, deaerated methylene chloride. The bottle was immediately pressurized to 207 kPa with ethylene. Ethylene was 15 continuously fed at 207 kPa with stirring at 23-25°C for 4 hr. After 4 hr, the ethylene feed was shut off and the reaction was stirred for 12 hr more. end of this time, the bottle was under zero pressure (gauge). The brown solution was rotary evaporated and 20 held under high vacuum to yield 5.15 g of thick, brown liquid polyethylene. 1H NMR analysis (CDCl3): 127 methyl carbons per 1000 methylene carbons. permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=20,200$; $M_w=32,100$; $M_w/M_n=1.59$.

Example 96

A 56-mg (0.066-mmol) sample of {[(2,6-i-PrPh)2DABMe2]PdCH2CH2C(0)CH3)}SbF6 was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 30 mL of dry, deaerated perfluoro(propyltetrahydrofuran). The autoclave was stirred and pressurized to 5.9 MPa with ethylene. The internal temperature peaked at 29°C; a cool water bath was placed around the autoclave body. The reaction was stirred for 16 hr at 23°C and 5.9 MPa and the ethylene was then vented. The autoclave contained a light

yellow granular rubber; this was scraped out of the autoclave and held under high vacuum to yield 29.0 g (15,700 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which had good elastic recovery and was very strong; it was soluble in chloroform or chlorobenzene.

The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of -57°C and a melting endotherm of -16°C 10 (35J/g) by differential scanning calorimetry. cooling, there was a crystallization exotherm with a maximum at 1° C (35J/g). Upon remelting and recooling the melting endotherm and crystallization exotherm persisted, as did the glass transition. 15 mechanical analysis at 1Hz showed a tan δ peak at -51°C and a peak in the loss modulus E" at -65°C; dielectric analysis at 1000 Hz showed a tan d peak at -35°C. NMR analysis (CDCl₃): 86 methyl carbons per 1000 methylene carbons. 13C NMR analysis: branching per 20 1000 CH₂: total Methyls (89.3), Methyl (37.2), Ethyl (14), Propyl (6.4), Butyl (6.9), ≥Am and End Of Chain (23.8); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene, 25 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=137,000; M_w=289,000; M_w/M_n=2.10.$ Intrinsic viscosity (trichlorobenzene, 135°C): 2.565 dL/g. Absolute molecular weight averages corrected for 30 branching: $M_n=196,000$; $M_w=425,000$; $M_w/M_n=2.17$. Density (determined at room temperature with a helium gas displacement pycnometer): 0.8546 ± 0.0007 g/cc.

Example 97

A 49-mg (0.058 mmol) sample of {{(2,6-i-35 PrPh)2DABMe1}PdCH2CH2C(0)CH3}SbF6 was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 30 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.9 MPa with ethylene.

The internal temperature peaked briefly at 34°C; a cool water bath was placed around the autoclave body. The reaction was stirred for 16 hr at 23°C. At 14 hr, the ethylene feed was shut off; the autoclave pressure dropped to 5.8 MPa over 2 hr; the ethylene was then vented. The autoclave contained a light yellow, gooey rubber swollen with hexane, which was scraped out of the autoclave and held under high vacuum to yield 28.2 g (17,200 catalyst turnovers) of spongy, non-tacky, rubbery polyethylene which had good elastic recovery and which was very strong.

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The polyethylene was amorphous at room temperature: it exhibited a glass transition temperature of -61°C and a melting endotherm of -12°C 15 (27J/g) by differential scanning calorimetry. Dynamic mechanical analysis at 1Hz showed a tan d peak at -52°C and a peak in the loss modulus E" at -70°C; dielectric analysis at 1000 Hz showed a tan d peak at -37°C. NMR analysis (CDCl₃): 93 methyl carbons per 1000 20 methylene carbons. 13C NMR analysis: branching per 1000 CHo: total Methyls (95.4), Methyl (33.3), Ethyl (17.2), Propyl (5.2), Butyl (10.8), Amyl (3.7), ≥Hex and End Of Chain (27.4); chemical shifts were referenced to the solvent: the high field carbon of 25 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): Mn=149,000; Mw=347,000; $M_W/M_{\rm n}$ =2.33. Density (determined at room temperature 30 with a helium gas displacement pycnometer): $0.8544 \pm$ 0.0007 g/cc.

Example 98

Approximately 10-mesh silica granules were dried at 200°C and were impregnated with a methylene chloride solution of $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(O)CH_3\}SbF_6$ to give a 10 wt% loading of the catalyst on silica.

A 0.53-g (0.063 mmol) sample of silica gel containing 10 wt% $\{[(2,6-i-$

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PrPh) 2DABMe2] PdCH2CH2C(O)CH3 SbF6 was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated hexane. The autoclave was stirred and pressurized to 5.5 MPa with ethylene; 5 the ethylene feed was then turned off. The internal temperature peaked briefly at 31°C. The reaction was stirred for 14 hr at 23°C as the pressure dropped to 5.3 MPa; the ethylene was then vented. The autoclave contained a clear, yellow, gooey rubber swollen with hexane. The product was dissolved in 200 mL chloroform, filtered through glass wool, rotary evaporated, and held under high vacuum to yield 7.95 g (4500 catalyst turnovers) of gummy, rubbery polyethylene. ¹H NMR analysis (CDCl₃): 96 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=6,900$; $M_w=118,000$; $M_W/M_{n}=17.08$.

Example 99

A 108-mg (0.073 mmol) sample of $\{[(2,6-i-$ PrPh) 2DABMe2 PdCH2CH2C(O)CH3 BAF was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added via syringe 75 mL of deaerated reagent grade methyl acrylate containing 100 ppm hydroquinone monomethyl ether and 100 ppm of phenothiazine. autoclave was pressurized to 5.5 MPa with ethylene and was stirred at 35°C as ethylene was continuously fed for 90 hr; the ethylene was then vented. The product consisted of a swollen clear foam wrapped around the impeller; 40 mL of unreacted methyl acrylate was poured off the polymer. The polymer was stripped off the impeller and was held under high vacuum to yield 38.2 g of clear, grayish, somewhat-tacky rubber. 1H NMR analysis (CDCl₃): 99 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain

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methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.9 mol% (2.6 wt%). This product yield and composition represent 18,400 ethylene turnovers and 158 methyl acrylate turnovers. ¹³C NMR analysis: branching per 1000 CH₂: .5 total Methyls (105.7), Methyl (36.3), Ethyl (22), Propyl (4.9), Butyl (10.6), Amyl (4), ≥Hex and End Of Chain (27.8), methyl acrylate (3.4); ester-bearing -CH(CH2)nCO2CH3 branches as a % of total ester: n≥5 (40.6), n=1,2,3 (2.7), n=0 (56.7); chemical shifts were 10 referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as 15 polymethylmethacrylate using universal calibration theory): $M_n=151,000$; $M_w=272,000$; $M_w/M_n=1.81$.

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Example 100

A 62-mg (0.074-mmol) sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}SbF_6$ was placed in a 20 600-mL Parr® stirred autoclave under nitrogen with 200 mL of deaerated aqueous 10% (v/v) n-butanol. autoclave was pressurized to 2.8 MPa with ethylene and was stirred for 16 hr. The ethylene was vented and the polymer suspension was filtered. The product consisted of a fine gray powdery polymer along with some larger 25 particles of sticky black polymer; the polymer was washed with acetone and dried to yield 0.60 g (290 catalyst turnovers) of polyethylene. The gray polyethylene powder was insoluble in chloroform at RT; it was soluble in hot tetrachloroethane, but formed a 30 gel on cooling to RT. 1H NMR analysis (tetrachloroethane-d2: 100°C): 43 methyl carbons per 1000 methylene carbons. Differential scanning calorimetry exhibited a melting point at 89°C (78J/g) with a shoulder at 70°C; there was no apparent glass 35 transition.

Example 101

A 78-mg (0.053-mmol) sample of $\{[(2,6-i-$ PrPh),DABMe, PdCH,CH,C(O)CH, BAF was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 40 mL of dry, deaerated t-butyl acrylate containing 100 ppm hydroquinone monomethyl ether. autoclave was pressurized with ethylene to 2.8 MPa and was stirred and heated at 35°C as ethylene was continuously fed at 2.8 MPa for 24 hr; the ethylene was then vented. The product consisted of a yellow, gooey 10 polymer which was dried under high vacuum to yield 6.1 g of clear, yellow, rubbery ethylene/t-butyl acrylate copolymer which was quite tacky. ¹H NMR analysis (CDCl₃): 102 methyl carbons per 1000 methylene carbons. Comparison of the integral of the ester t-butoxy (1.44 15 ppm) peak with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a t-butyl acrylate content of 0.7 mol% (3.3 This yield and composition represent 3960 ethylene turnovers and 30 t-butyl acrylate turnovers. 20 Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=112,000$; $M_w=179,000$; $M_w/M_n=1.60$.

Example 102

25 A 19-mg (0.022-mmol) sample of { [(2,6-i-PrPh)2DABMe2] PdCH2CH2C(0) CH3 } SbF6 was placed in a 600-mL Parr® stirred autoclave under nitrogen. autoclave was pressurized to 5.2 MPa with ethylene and was stirred for 2 hr; the ethylene feed was then shut 30 off. The autoclave was stirred for 16 hr more as the ethylene pressure dropped to 5.0 MPa; the ethylene was then vented. The autoclave contained a light yellow, granular sponge rubber growing all over the walls and head of the autoclave; this was scraped out to yield 13.4 g (21,800 catalyst turnovers) of spongy, nontacky, rubbery polyethylene which was very strong and ¹H NMR analysis (CDCl₃): 90 methyl carbons per 1000 methylene carbons.

Differential scanning calorimetry exhibited a glass transition at -50°C. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=175,000$; $M_w=476,000$; $M_w/M_n=2.72$.

Example 103

A 70-mg (0.047-mmol) sample of $\{[(2,6-i-$ PrPh) 2DABMe2] PdCH2CH2C(O)CH3 BAF was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was 10 added 70 mL of deaerated reagent grade methyl acrylate containing 100 ppm each hydroquinone monomethyl ether and phenothiazine and 0.7 mL (1 wt%; 4.7 mol%) deaerated, deionized water. The autoclave was stirred at 35°C as ethylene was continuously fed at 4.8 MPa for 15 16 hr; the ethylene was then vented. The product consisted of a clear solution. Rotary evaporation yielded 1.46 g of ethylene/methyl acrylate copolymer as a clear oil. The infrared spectrum of the product 20 exhibited a strong ester carbonyl stretch at 1740cm⁻¹. ¹H NMR analysis (CDCl₃): 118 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain 25 methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 0.7 mol% (2.2 wt%). This product yield and composition represent 1090 ethylene turnovers and 8 methyl acrylate turnovers. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, 30 results calculated as polyethylene using universal calibration theory): $M_n=362$; $M_w=908$; $M_w/M_n=2.51$.

Example 104

A 53-mg (0.036-mmol) sample of {[(2,6-i-35 PrPh)₂DABMe₂}PdCH₂CH₂C(O)CH₃}BAF was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 100 mL of dry, deaerated methylene chloride. The autoclave was immersed in a cool water bath and stirred

as it was pressurized to 4.8 MPa with ethylene. Ethylene was continuously fed with stirring at 4.8 MPa and 23°C for 23 hr; the ethylene then was vented. The product consisted of a clear rubber, slightly swollen with methylene chloride. The polymer was dried under high vacuum at room temperature to yield 34.5 g (34,100 catalyst turnovers) of clear rubbery polyethylene. ¹H NMR analysis (CDCl₃): 110 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M_n=243,000; M_w=676,000; M_w/M_n=2.78.

Example 104

15 A 83-mg (0.056-mmol) sample of $\{(2,6-i-$ PrPh) DABMe] PdCH2CH2C(O)CH3 BAF was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 70 mL of dry, deaerated, ethanol-free chloroform. The autoclave was immersed in a cool water bath and 20 stirred as it was pressurized to 4.7 MPa with ethylene. Ethylene was continuously fed with stirring at 4.7 MPa and 23°C for 21 hr; the ethylene then was vented. product consisted of a pink, rubbery, foamed polyethylene, slightly swollen with chloroform. polymer was dried under vacuum at 40°C to yield 70.2 g (44,400 catalyst turnovers) of pink, rubbery polyethylene which was slightly tacky. 1H NMR analysis (CDCl₃): 111 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as 30 polyethylene using universal calibration theory): $M_n = 213,000; M_w = 728,000; M_w/M_n = 3.41.$

Example 105

A 44-mg (0.052-mmol) sample of {{(2,6-i-35 PrPh)₂DABMe₂]PdCH₂CH₂C(O)CH₃}SbF₆ was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 20 mL of dry, deaerated methylene chloride. To this was added 5 mL (5.25 g; 73 mmol) of freshly distilled

acrylic acid (contains a few ppm of phenothiazine as a radical polymerization inhibitor) via syringe and the mixture was immediately pressurized with ethylene at 5.52 kPa and stirred for 40 hr. The dark yellow solution was rotary evaporated and the residue was stirred with 50 mL water for 15 min to extract any acrylic acid homopolymer. The water was drawn off with a pipette and rotary evaporated to yield 50 mg of dark residue. The polymer which had been water-extracted was heated under high vacuum to yield 1.30 g of

was heated under high vacuum to yield 1.30 g of ethylene/acrylic acid copolymer as a dark brown oil. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at 1705cm⁻¹, as well as strong methylene absorbances at 3000-2900 and 1470cm⁻¹.

15 A 0.2-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum of the esterified copolymer showed a strong ester carbonyl absorbance at 1750cm⁻¹; the COOH absorbances were gone. 1H NMR analysis (CDCl₃): 87 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the

2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 5.3 mol% (14.7 wt% methyl acrylate => 12.3 wt% acrylic acid in the original copolymer). This product yield and composition represent 780 ethylene turnovers and 43 acrylic acid turnovers. Gel permeation chromatography

ester methoxy (3.67ppm) and ester methylene (CH2COOMe;

(tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=25,000$; $M_w=42,800$; $M_w/M_n=1.71$.

Listed below are the ¹³C NMR data upon which the above analysis is based.

13C NMR Data CDCl₃, 0.05M CrAcAc, 3OC

Freq ppm Intensity

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51.0145	24.9141	
45.434	1.11477	MEB _O
38.8925	2.29147	
38.5156	6.51271	
37.3899	10.7484	
37.0713	17.3903	
36.7634	17.6341	
36.4182	3.57537	•
36.2961	6.0822	
34.459	2.158	
34.0289	9.49713	
33.7369	34.4456	
33.3705	49.2646	
32.8926	18.2918	
32.3935	10.5014	
32.0271	3.5697	3B ₅
31.5705	30.6837	3B ₆ +, 3EOC
31.1723	1.54526	6
29.813	46.4503	
29.3511	117.987	
29.1387	21.034	
28.9953	30.603	
28.613	7.18386	•
27.2007	8.02265	
26.744	23.8731	
26.3777	46.8498	
26.006	5.42389	
25.5547	8.13592	•
25.0609	5.46013	2 EB ₄ (tentative)
24.9175	2.30355	2 EB ₄ (tentative)
24.6042	15.7434	2 EB ₅ +
23.7547	2.78914	5
23.3777	5.63727	
22.7936	8.07071	2B ₄
22.6768	3.78032	2B ₄
22.3211	33.1603	2B ₅ +, 2EOC
19.3477	15.4369	181
18.8645	5.97477	181
14.1814	1.99297	1B ₃
13.7407	38.5361	1B ₄ +, 1EOC
11.0274	6.19758	1B ₂
10.5124	10.4707	1B ₂
176.567	9.61122	EB ₀ carbonyl
174.05	9.03673	EB ₁ + carbonyl
173.779	85.021	EB ₁ + carbonyl
	00.021	

Example 106

A 25-mg (0.029-mmol) sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(0)CH_3\}SbF_6$ was magnetically stirred under 55.2 kPa of ethylene in a 50-mL Schlenk flask with 20 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 40 hr at room temperature. The yellow solution was rotary 204

evaporated to yield 3.41 g of ethylene/methyl 4pentenoate copolymer as a yellow oil. The infrared spectrum of the copolymer showed a strong ester carbonyl absorbance at 1750cm⁻¹. ¹H NMR analysis (CDCl₃): 84 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl 4-pentencate content of 6 mol% (20 wt%). This yield 10 and composition represent about 3400 ethylene turnovers and 200 methyl 4-pentenoate turnovers. 13C NMR branching per 1000 CH2: total quantitative analysis: Methyls (93.3), Methyl (37.7), Ethyl(18.7), Propyl (2), Butyl (8.6), ≥Am and end of chains (26.6), ≥Bu and end 15 of chains (34.8); ester-bearing branches -CH(CH₂)_nCO₂CH₃ as a % of total ester: $n \ge 5$ (38.9), n = 4 (8.3), n = 1, 2, 3(46.8), n=0 (6); chemical shifts were referenced to the solvent: chloroform-d1 (77 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, 20 polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=32,400$; $M_w=52,500$; $M_w/M_n=1.62$.

Example 107

A 21-mg (0.025-mmol) sample of $\{[(2,6-i-$ 25 PrPh) 2DABMe2] PdCH2CH2C(O)CH3}SbF6 was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 5 mL of dry methylene chloride and 5 mL (4.5 g; 39 mmol) of methyl 4-pentenoate for 74 hr. The yellow solution was rotary evaporated to yield 0.09 g of a yellow oil, 30 poly[methyl 4-pentenoate]. The infrared spectrum showed a strong ester carbonyl absorbance at 1750cm-1. The $^1\mathrm{H}$ NMR (CDCl₃) spectrum showed olefinic protons at 5.4-5.5ppm; comparing the olefin integral with the integral of the ester methoxy at 3.67ppm indicates an 35 average degree of polymerization of 4 to 5. example demonstrates the ability of this catalyst to

'iomopolymerize alpha olefins bearing polar'functional groups not conjugated to the carbon-carbon double bond.

Example 108

A 53-mg (0.063-mmol) sample of $\{(2,6-i-$

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PrPh) 2DABMe; PdCH2CH2C(O)CH3 SbF6 was placed in a 600-mL Parr® stirred autoclave under nitrogen. To this was added 25 mL of dry, deaerated toluene and 25 mL (26 g; 0.36 mol) of freshly distilled acrylic acid containing about 100 ppm phenothiazine. The autoclave was pressurized to 2.1 MPa with ethylene and was stirred for 68 hr at 23°C; the ethylene was then vented. autoclave contained a colorless, hazy solution. solution was rotary evaporated and the concentrate was taken up in 50 mL of chloroform, filtered through diatomaceous earth, rotary evaporated, and then held under high vacuum to yield 2.23 g of light brown, very viscous liquid ethylene/acrylic acid copolymer. The infrared spectrum showed strong COOH absorbances at 3400-2500 and at $1705cm^{-1}$, as well as strong methylene absorbances at 3000-2900 and 1470cm^{-1} .

A 0.3-g sample of the ethylene/acrylic acid copolymer was treated with diazomethane in ether to esterify the COOH groups and produce an ethylene/methyl acrylate copolymer. The infrared spectrum showed a strong ester carbonyl absorbance at 1750cm⁻¹; the COOH absorbances were gone. 1H NMR analysis (CDCl3): 96 methyl carbons per 1000 methylene carbons. of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 1.8 mol% (5.4 wt% methyl acrylate => 4.5 wt% acrylic acid in the original copolymer). This product yield and composition represent 1200 ethylene turnovers and 22 acrylic acid turnovers. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using

universal calibration theory): $M_n=5,330$; $\overline{M}_w=\overline{15},000$; $M_w/M_n=2.82$.

Example 109

A 600-mL stirred Parr® autoclave was sealed and flushed with nitrogen. Fifty mL (48 g; 0.56 mol) of 5 dry, deaerated methyl acrylate was introduced into the autoclave via gas tight syringe through a port on the autoclave head. Then 60 mg (0.07 mmol) of $\{(2,6-i-$ PrPh) 2DABMe2] PdMe(Et20) BAF was introduced into the 10 autoclave in the following manner: a 2.5-mL gas tight syringe with a syringe valve was loaded with 60 mg of {[(2,6-i-PrPh)2DABMe2]PdMe(Et2O)}BAF under nitrogen in a glove box; then 1 mL of dry, deaerated methylene chloride was drawn up into the syringe and the contents were quickly injected into the autoclave through a head 15 This method avoids having the catalyst in solution with no stabilizing ligands.

The autoclave body was immersed in a running tap water bath; the internal temperature was very steady at 22°C. The autoclave was pressurized with ethylene to 20 2.8 MPa and continuously fed ethylene with stirring for 4.5 hr. The ethylene was then vented and the product, a mixture of methyl acrylate and yellow gooey polymer, was rinsed out of the autoclave with chloroform, rotary evaporated, and held under high vacuum overnight to 25 yield 4.2 g of thick, light-brown liquid ethylene/methyl acrylate copolymer. The infrared spectrum of the product exhibited a strong ester carbonyl stretch at 1740cm⁻¹. ¹H NMR analysis (CDCl₃): 30 82 methyl carbons per 1000 methylene carbons. Comparison of the integrals of the ester methoxy (3.67ppm) and ester methylene (CH2COOMe; 2.30ppm) peaks with the integrals of the carbon chain methyls (0.8-0.9ppm) and methylenes (1.2-1.3ppm) indicated a methyl acrylate content of 1.5 mol% (4.4 wt%). This product 35 yield and composition represent 2000 ethylene turnovers and 31 methyl acrylate turnovers. 13C NMR analysis: branching per 1000 CH2: total Methyls (84.6), Methyl

(28.7), Ethyl (15.5), Propyl (3.3), Butyl (8.2), \geq Hex-and End Of Chain (23.9), methyl acrylate (13.9). Esterbearing -CH(CH2)_nCO2CH3 branches as a % of total ester: $n\geq 5$ (34.4), n=4 (6.2), n=1,2,3 (13), n=0 (46.4). Mole%: ethylene (97.6), methyl acrylate (2.4); chemical shifts were referenced to the solvent: the high field carbon of 1,2,4-trichlorobenzene (127.8 ppm). Gel permeation chromatography (tetrahydrofuran, 30°C, polymethylmethacrylate reference, results calculated as polymethylmethacrylate using universal calibration theory): $M_n=22,000$; $M_w=45,500$; $M_w/M_n=2.07$.

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A mixture of 1.45 g of this ethylene/methyl acrylate copolymer, 20 mL dioxane, 2 mL water, and 1 mL of 50% aqueous NaOH was magnetically stirred at reflux under nitrogen for 4.5 hr. The liquid was then decanted away from the swollen polymer and the polymer was stirred several hours with three changes of boiling The polymer was filtered, washed with water and methanol, and dried under vacuum (80°C/nitrogen purge) to yield 1.2 g soft of ionomer rubber, insoluble in hot The FTIR-ATR spectrum of a pressed film chloroform. (pressed at 125°C/6.9 MPa) showed a strong ionomer peak at 1570cm⁻¹ and virtually no ester carbonyl at 1750cm⁻ The pressed film was a soft, slightly tacky rubber with about a 50% elongation to break. This example demonstrates the preparation of an ionomer from this ethylene/methyl acrylate polymer.

Example 110

The complex [(2,6-i-PrPh)2DABMe2]PdMeCl (0.020 g, 0.036 mmol) was weighed into a vial and dissolved in 6 ml CH2Cl2. NaBAF (0.032g, 0.036 mmol) was rinsed into the stirring mixture with 4 ml of CH2Cl2. There was an immediate color change from orange to yellow. The solution was stirred under 6.2 MPa ethylene in a Fisher Porter tube with temperature control at 19°C. The internal temperature rose to 22°C during the first 15 minutes. The temperature controller was raised to 30°C. After 35 minutes, the reaction was consuming

thylene slowly. After a total reaction time of about 20 h, there was no longer detectable ethylene consumption, but the liquid level in the tube was noticeably higher. Workup by addition to excess MeOH gave a viscous liquid precipitate. The precipitate was redissolved in CH2Cl2, filtered through a 0.5 micron PTFE filter and reprecipitated by addition to excess MeOH to give 7.208 g dark brown viscous oil (7180 equivalents of ethylene per Pd). 1H NMR (CDCl3) 0.8-10 (m, CH3); 1.0-1.5 (m, CH and CH2). Integration allows calculation of branching: 118 methyl carbons per 1000 methylene carbons. GPC in THF vs. PMMA standard: Mn=12,700, Mw=28,800, Mw/Mn=2.26.

Example 111

15 The solid complex $\{[(2,6-i PrPh)_2DABMe_2$ PdMe(Et₂O) SbF_6 (0.080 g, 0.096 mmol) was placed in a Schlenk flask which was evacuated and refilled with ethylene twice. Under one atm of ethylene, black spots formed in the center of the solid 20 complex and grew outward as ethylene was polymerized in the solid state and the resulting exotherm destroyed the complex. Solid continued to form on the solid catalyst that had not been destroyed by the exotherm, and the next day the flask contained considerable solid and the reaction was still slowly consuming ethylene. The ethylene was disconnected and 1.808 g of light gray elastic solid was removed from the flask (644 equivalents ethylene per Pd). The 1H NMR in CDCl3 was similar to example 110 with 101 methyl carbons per 1000 methylene carbons. Differential Scanning Calorimetry 30 (DSC): first heat 25 to 150°C, 15°C/min, no events; second heat -150 to 150 °C, $T_q = -53$ °C with an endothermic peak centered at -20°C; third heat -150 to 2.75 °C, $T_{q} = -51$ °C with an endothermic peak centered at -20°C. GPC (trichlorobenzene, 135°C, polystyrene 35 reference, results calculated as linear polyethylene using universal calibration theory): $M_n=13,000$ $M_{w}=313,000 \quad M_{w}/M_{n}=24.$

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Example 11

The complex {[(2,6-i-PrPh),DABMe,]PdMe(Et,O)}SbF₆ (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry dioxane. septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. 10 A room temperature water bath was used to control the temperature of the reaction. After 20 h, the reaction was worked up by removing the solvent in vacuo to give 10.9 g of a highly viscous fluid (3870 equivalents of ethylene per Pd). Dioxane is a solvent for the Pd 15 complex and a non-solvent for the polymer product. NMR (CDCl₃) 0.8-1.0 (m, CH₃); 1.0-1.5 (m, CH and CH₂). Integration allows calculation of branching: 100 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene, 135°C, polystyrene reference, 20 results calculated as linear polyethylene using universal calibration theory): Partially resolved trimodal distribution with $M_n=16300$, $M_w=151000$ $M_W/M_D=9.25$. DSC (second heat, -150°C to 150°C, 15°C/min) T_G=-63°C, endothermic peak centered at -25 30°C.

Example 113

Polymerization of ethylene was carried out according to example 112, using pentane as solvent. Pentane is a non-solvent for the Pd complex and a solvent for the polymer product. The reaction gave 7.47 g of dark highly viscous fluid (2664 equivalents of ethylene per Pd). 1H NMR analysis (CDCl3): 126 methyl carbons per 1000 methylene carbons. 13C NMR analysis, branching per 1000 CH2: Total methyls (128.8), Methyl (37.8), Ethyl (27.2), Propyl (3.5), Butyl (14.5), Amyl (2.5), >Hexyl and end of chain (44.7), average number of carbon atoms for >Hexyl branches = 16.6 (calculated from intrinsic viscosity

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and GPC molecular weight data). Quantitation of the - $\mathrm{CH_2CH}(\mathrm{CH_3})\,\mathrm{CH_2CH_3}$ structure per 1000 $\mathrm{CH_2}$'s: 8.3. These side chains are counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis. GPC

branch in the quantitative branching analysis. GPC

5 (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): Mn=9,800, Mw=16,100, Mw/Mn=1.64. Intrinsic viscosity (trichlorobenzene, 135°C) = 0.125 g/dL. Absolute molecular weights

10 calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): Mn=34,900, Mw=58,800, Mw/Mn=1.68.

DSC (second heat, -150°C to 150°C, 15°C/min) Tg = -71°C, endothermic peak centered at -43°C.

Example 114

Polymerization of ethylene was carried out according to example 112, using distilled degassed water as the medium. Water is a non-solvent for both the Pd complex and the polymer product. The mixture was worked up by decanting the water from the product which was then dried in vacuo to give 0.427 g of dark sticky solid (152 equivalents of ethylene per Pd). 1 H NMR analysis (CDCl₃): 97 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_{\rm D}=25,100$, $M_{\rm W}=208,000$, $M_{\rm W}/M_{\rm D}=8.31$.

Example 115

Polymerization of ethylene was carried out according to example 112, using 2-ethylhexanol as the solvent. The Pd complex is sparingly soluble in this solvent and the polymer product is insoluble. The polymer product formed small dark particles of high viscosity liquid suspended in the 2-ethylhexanol. The solvent was decanted and the polymer was dissolved in CHCl3 and reprecipitated by addition of excess MeOH. The solvent was decanted, and the reprecipitated polymer was dried in vacuo to give 1.66 g of a dark

ighly viscous fluid (591 equivalents of ethylene per Pd). 1 H NMR analysis (CDCl₃): 122 methyl carbons per 1000 methylene carbons. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_{n}=7,890$, $M_{w}=21,600$, $M_{w}/M_{n}=2.74$.

Example 116

The solid complex {[(2,6-i-PrPh) 2DABMe2] PdMe (Et2O) }SbF6 (0.084 g, 0.100 mmol) was 10 loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to -78°C. Solvent, (CH₂Cl₂, 40 ml) was added by syringe and after equilibrating at -78°C under ethylene, the mixture was warmed to room 15 temperature under ethylene. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. There was rapid uptake of ethylene. A room temperature water bath was used to control the temperature of the reaction. After 24 h, 20 the reaction was worked up by removing the solvent in vacuo to give 24.5 g of a highly viscous fluid (8730 equivalents of ethylene per Pd). CH2Cl2 is a good solvent for both the Pd complex and the polymer product. The polymer was dissolved in CH2Cl2, and 25 reprecipitated by addition to excess MeOH in a tared The solvent was decanted, and the reprecipitated polymer was dried in vacuo to give 21.3 g of a dark highly viscous fluid. 1H NMR analysis (CDCl₃): 105 methyl carbons per 1000 methylene carbons. 30 C-13 NMR analysis, branching per 1000 CH2: Total methyls (118.6), Methyl (36.2), Ethyl (25.9), Propyl (2.9), Butyl (11.9), Amyl (1.7), ≥Hexyl and end of chains (34.4), average number of carbon atoms for ≥ Hexyl branches = 22.5 (calculated from intrinsic viscosity and GPC molecular weight data). Quantitation 3.5 of the -CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 8.1. These side chains also counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis.

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- GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=25,800$, $M_w=45,900$, $M_w/M_n=1.78$. Intrinsic viscosity (trichlorobenzene,
- 5 135°C) = 0.24 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): $M_{\rm D}=104,000$, $M_{\rm W}=188,000$, $M_{\rm W}/M_{\rm D}=1.81$.
- 10 Listed below are the ¹³C NMR data upon which the above analysis is based.

13C NMR Data TCB, 120C, 0.06M CrAcAc

		20C, U.USM CTACAC
Freq ppm	Intensity	
39.7233	5.12305	
39.318	17.6892	MB ₂
38.2022	17.9361	MB ₃ +
37.8369	32.3419	MB ₃ +
37.2469	43.1136	αB_1 , $3B_3$
36.8335	10.1653	αB_1 , $3B_3$
36.7452	14.674	αB_1 , $3B_3$
34.9592	10.3554	$\alpha\gamma+B$, $(4B_4$, $5B_5$, etc.)
34.6702	24.015	$\alpha\gamma+B$, $(4B_4$, $5B_5$, etc.)
34.5257	39.9342	αγ+B, (4B ₄ , 5B ₅ , etc.)
34.2006	109.158	$\alpha\gamma + B$, $(4B_4$, $5B_5$, etc.)
33.723	36.1658	$\alpha y + B$, (4B ₄ , 5B ₅ , etc.)
33.3136	12.0398	MB ₁
32.9323	20.7242	MB ₁
32.4266	6.47794	3B ₅
31.9409	96.9874	3B ₆ +, 3EOC
31.359	15.2429	γ+γ+Β, 3B ₄
31.0981	19.2981	γ+γ+B, 3B ₄
30.6606	15.8689	γ+γ+B, 3B ₄
30.2271	96.7986	γ+γ+B, 3B ₄
30.1188	54.949	y+y+B, 3B ₄
29.7455	307.576	γ+γ+B, 3B ₄
29.5809	36.2391	γ+γ+B, 3B ₄
29.3361	79.3542	γ+γ+Β, 3B ₄
29.2157	23.0783	γ+γ+B, 3B ₄
27.6424	24.2024	βγ+B, 2B ₂ ,(4B ₅ , etc.)
27.526	29.8995	βγ+B, 2B ₂ ,(4B ₅ , etc.)
27.3534	23.1626	$\beta \gamma + B$, $2B_2$, $(4B_5$, etc.)
27.1607	70.8066	$\beta \gamma + B$, $2B_2$, $(4B_5$, etc.)
27.0042	109.892	$\beta \gamma + B$, $2B_2$, $(4B_5$, etc.)
26.5908	7.13232	βγ+B, 2B ₂ ,(4B ₅ , etc.)
26.3941	23.945	$\beta \gamma + B$, $2B_2$, $(4B_5$, etc.)
25.9446	4.45077	βγ+B, 2B ₂ ,(4B ₅ , etc.)
24.4034	9.52585	ββв
24.2428	11.1161	ββв
23.1391	21.2608	2B ₄
23.0227	11.2909	2B ₄
22.6494	103.069	2B ₅ +, 2EOC
20.0526	5.13224	2B ₃
19.7355	37.8832	1B ₁
19.2017	14.8043	1B ₁ , Structure XXVII
14.4175	4.50604	1B ₃ 1B ₄ +, 1EOC
13.9118	116.163	_ _ _ *
11.1986	18.5867 32.3855	^{1B} 2, Structure XXVII 1B ₂
10.9617	34.3633	±02

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Example 117

Polymerization of ethylene was carried out according to example 116, at a reaction temperature of 0°C and reaction time of several hours. The polymer 5 product formed a separate fluid phase on the top of the The reaction was quenched by adding 2 ml acrylonitrile. The product was moderately viscous 1_H fluid, 4.5 g (1600 equivalents of ethylene per Pd). NMR analysis (CDCl₃): 108 methyl carbons per 1000 10 methylene carbons. 13C NMR analysis, branching per 1000 CH2: Total methyls (115.7), Methyl (35.7), Ethyl (24.7), Propyl (2.6), Butyl (11.2), Amyl (3.2), ≥Hexyl and end of chain (37.1). Quantitation of the -CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 7.0. These 15 side chains are counted as a Methyl branch and an Ethyl branch in the quantitative branching analysis. (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: $M_n=15,200$, $M_w=23,700$, 20 $M_W/M_{n}=1.56$.

Example 118

The Pd complex {[(2,6-i- $PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(0)OCH_3\}SbF_6^*(0.084 g, 0.100)$ mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of FC-75 was added. The septum-capped flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. Both the Pd initiator and the polymer are insoluble in FC-75. After 15 days, the reaction flask contained a large amount of gray elastic solid. The FC-75 was decanted, and the solid polymer was then dissolved in CHCl3 and precipitated by addition of the solution to excess MeOH. The polymer was dried in vacuo, and then dissolved in o-dichlorobenzene at The hot solution was filtered through a 10 μm PTFE filter. The filtered polymer solution was shaken

in a separatory funnel with concentrated sulfuric acid, followed by distilled water, followed by 5% NaHCO3 solution, followed by two water washes. The polymer appeared to be a milky suspension in the organic layer 5 during this treatment. After washing, the polymer was precipitated by addition to excess MeOH in a blender and dried at room temperature in vacuo to give 19.6 g light gray elastic polymer fluff (6980 equivalents of ethylene per Pd). 1H NMR analysis (CDCl3): 112 methyl carbons per 1000 methylene carbons. 13C NMR analysis, 10 branching per 1000 CH2: Total methyls (114.2), Methyl (42.1), Ethyl (24.8), Propyl (5.1), Butyl (10.2), Amyl (4), ≥Hexyl and end of chain (30.3), average number of carbon atoms for ≥Hexyl branches = 14.4 (calculated 15 from intrinsic viscosity and GPC molecular weight data). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory: $M_n=110,000$, $M_W=265,000$, $M_W/M_D=2.40$. Intrinsic viscosity 20 (trichlorobenzene, 135°C) = 1.75 g/dL. Absolute molecular weights calculated by GPC (trichlorobenzene, . 135°C, polystyrene reference, corrected for branching using measured intrinsic viscosity): Mn=214,000, $M_{W}=535,000, M_{W}/M_{\Pi}=2.51.$

25 Example 119

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Polymerization of ethylene was carried out according to example 112, using the complex $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(0)OCH_3\}SbF_6$ (0.084 g, 0.100 mmol) as the initiator and CHCl3 as the solvent. The reaction gave 28.4 g of dark viscous fluid (10,140 equivalents of ethylene per Pd). 1H NMR analysis (CDCl3): 108 methyl carbons per 1000 methylene carbons. 13C NMR analysis, branching per 1000 CH2: Total methyls (119.5), Methyl (36.9), Ethyl (25.9), Propyl (2.1), Butyl (11), Amyl (1.9), \geq Hexyl and end of chain (38.9). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene

universal calibration theory): $M_n=10,800$, $M_w=26,800$, $M_w/M_n=2.47$.

Example 120

Polymerization of ethylene was carried out

according to example 112, using the complex [(2,6-i-PrPh)₂DABMe₂]PdMe(OSO₂CF₃) (0.068g, 0.10 mmol) as the initiator and CHCl₃ as the solvent. The reaction gave 5.98 g of low viscosity fluid (2130 equivalents of ethylene per Pd). ¹H NMR (CDCl₃) 0.8-1.0 (m, CH₃);

10 1.0-1.5 (m, CH and CH₂); 1.5-1.7 (m, CH₃CH=CH-); 1.9-2.1 (broad, -CH₂CH=CHCH₂-); 5.3-5.5 (m, -CH=CH-). Integration of the olefin end groups assuming one olefin per chain gives M₁ = 630 (DP = 24). A linear polymer with this molecular weight and methyl groups at both ends should have 46 methyl carbons per 1000 methylene carbons. The value measured by integration is 161, thus this polymer is highly branched.

Example 121

Polymerization of ethylene was carried out according to example 112, using the complex {[(2,6-i-20 PrPh) 2DABH2 PdCH2CH2CH2C(0)OCH3 SbF6 (0.082 g, 0.10 mmol) as the initiator and CHCl3 as the solvent. The reaction gave 4.47 g of low viscosity fluid (1600 equivalents of ethylene per Pd). 1H NMR (CDCl3) is similar to example 120. Integration of the olefin end 25 groups assuming one olefin per chain gives $M_{\rm n}$ = 880 (DP = 31). A linear polymer with this molecular weight and methyl groups at both ends should have 34 methyl carbons per 1000 methylene carbons. The value measured by integration is 156, thus this polymer is highly 30 branched.

Example 122

Polymerization of ethylene was carried out according to example 112, using the complex $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(0)OCH_3\}BCl(C_6F_5)_3$ (0.116 g, 0.10 mmol) as the initiator and CHCl3 as the solvent. The reaction gave 0.278 g of low viscosity fluid, after correcting for the catalyst residue this is 0.160 g (57)

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equivalents of ethylene per Pd). M_n estimated by integration of olefin end groups is 300.

Example 123

The complex [(2,6-i-PrPh)₂DABMe₂]PdMeCl (0.056 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox followed by 40 ml of dry toluene. A solution of ethyl aluminum dichloride (1.37 ml of 0.08 M solution in o-dichlorobenzene) was added while stirring. Polymerization of ethylene was carried out using this solution according to example 112. The reaction gave 0.255 g of low viscosity fluid, after correcting for the catalyst residue this is 0.200 g (71 equivalents of ethylene per Pd). Mn estimated by integration of olefin end groups is 1300.

15 Example 124

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The solid complex {[(2,6-i-

- 20 PrPh)₂DABMe₂] PdMe(Et₂O)}SbF₆ (0.084 g, 0.100 mmol) was loaded into a Schlenk flask in the drybox. The flask was connected to a Schlenk line under 1 atm of ethylene, and cooled to -78°C. Forty ml of CH₂Cl₂ was added by syringe and after equilibrating at -78°C under
- ethylene, 5 ml of methyl acrylate was added by syringe and the mixture was warmed to room temperature under ethylene. After 40 h, the reaction was worked up by removing the solvent in vacuo to give 3.90 g of moderately viscous fluid. Integration of the ¹H NMR spectrum showed that this copolymer contained 6.9 mole
 - % methyl acrylate. No poly(methyl acrylate)
 homopolymer could be detected in this sample by ¹H NMR.
 ¹H NMR shows that a significant fraction of the ester
 groups are located at the ends of hydrocarbon branches:
- 35 3.65(s, $-CO_2CH_3$, area=4.5), 2.3(t, $-CH_2CO_2CH_3$, ester ended branches, area=3), 1.6(m, $-CH_2CH_2CO_2CH_3$, esterended branches, area=3), 0.95-1.55(m, CH and other CH₂, area=73), 0.8-0.95(m, CH₃, ends of branches or ends of

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chains, area=9.5) This is confirmed by the ¹³C NMR quantitative analysis: Mole%: ethylene (93.1), methyl acrylate (6.9), Branching per 1000 CH₂: Total methyls (80.2), Methyl (30.1), Ethyl (16.8), Propyl (1.6),

Butyl (6.8), Amyl (1.3), \geq Hexyl and end of chain (20.1), methyl acrylate (41.3), Ester branches CH(CH₂)_nCO₂CH₃ as a % of total ester: n \geq 5 (47.8), n=4 (17.4), n=1,2,3 (26.8), n=0 (8).

GPC of this sample was done in THF vs. PMMA

10 standards using a dual UV/RI detector. The outputs of
the two detectors were very similar. Since the UV
detector is only sensitive to the ester functionality,
and the RI detector is a relatively nonselective mass
detector, the matching of the two detector outputs

15 shows that the ester functionality of the methyl
acrylate is distributed throughout the entire molecular
weight range of the polymer, consistent with a true
copolymer of methyl acrylate and ethylene.

A 0.503 g sample of the copolymer was fractionated 20 by dissolving in benzene and precipitating partially by slow addition of MeOH. This type of fractionation experiment is a particularly sensitive method for detecting a low molecular weight methyl acrylate rich component since it should be the most soluble material 25 under the precipitation conditions.

The precipitate 0.349 g, (69%) contained 6.9 mole % methyl acrylate by ^1H NMR integration, GPC (THF, PMMA standard, RI detector): $M_n = 19,600$, $M_w = 29,500$, $M_w/M_n = 1.51$. The soluble fraction 0.180g (36%) contained 8.3 mole % methyl acrylate by ^1H NMR integration, GPC (THF, PMMA standard, RI detector): $M_n = 11,700$, $M_w = 19,800$, $M_w/M_n = 1.70$. The characterization of the two fractions shows that the acrylate content is only slightly higher at lower molecular weights. These results are also consistent with a true copolymer of the methyl acrylate with ethylene.

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Example 125

Methyl acrylate was sparged with argon, dried over activated 4A sieves, passed through activity 1 alumina B in the drybox, and inhibited by addition of 20 ppm phenothiazine. The complex [(2,6-i-5 $PrPh)_2DABMe_2]PdMe(OSO_2CF_3)$ (0.068 g, 0.10 mmol) was loaded into a Schlenk flask in the drybox, and 40 ml of CHCl₃ was added followed by 5 ml of methyl acrylate.. The septum capped flask was connected to a Schlenk line 10 and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. The light orange mixture was stirred under an ethylene atmosphere at slightly above 1 atm by using a mercury bubbler. After 20 h, the reaction was worked up by removing the 1.5 solvent and unreacted methyl acrylate in vacuo to give 1.75 g of a low viscosity copolymer.

13C NMR quantitative analysis: Mole%: ethylene (93), methyl acrylate (7), Branching per 1000 CH₂: Total methyls (100.9), Methyl (33.8), Ethyl (19.8),
20 Propyl (1.9), Butyl (10.1), Amyl (7.3), ≥Hexyl and end of chains (28.4), methyl acrylate (41.8). This sample is low molecular weight - total methyls does not include end of chain methyls. Ester branches - CH(CH₂)_nCO₂CH₃ as a % of total ester: n≥5 (51.3), n=4 (18.4), n=1,2,3 (24), n=0 (6.3).

Example 126

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(0)OCH_3\}BAF$ (0.136 g, 0.10 mmol) in CH_2Cl_2 solvent with a reaction time of 72 hours to give 4.93 g of copolymer.

Example 127

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)2DABMe2]PdCH2CH2CH2C(0)OCH3}SbF6 (0.084 g, 0.10 mmol) with a reaction time of 72 hours to give 8.19 g of copolymer.

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Example 128

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst {[(2,6-i-PrPh)2DABH2]PdCH2CH2CH2C(O)OCH3}SbF6 (0.082 g, 0.10 mmol) to give 1.97 g of copolymer.

Example 129

Ethylene and methyl acrylate were copolymerized according to example 125 with catalyst $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(CH_3CN)\}SbF_6$ (0.080 g, 0.10 mmol) to give 3.42 g of copolymer. The ¹H NMR shows primarily copolymer, but there is also a small amount of poly(methyl acrylate) homopolymer.

Example 130

Ethylene and methyl acrylate (20 ml) were

copolymerized in 20 ml of CHCl₃ according to example

125 using catalyst {[(2,6-iPrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆ (0.339 g, 0.40

mmol) to give 2.17 g of copolymer after a reaction time
of 72 hours. ¹³C NMR quantitative analysis: Mole%:

ethylene (76.3), methyl acrylate (23.7). Branching per
1000 CH₂: Total methyls (28.7), Methyl (20.5), Ethyl
(3.8), Propyl (0), Butyl (11), ≥Amyl and end of chains
(13.6), methyl acrylate (138.1). Ester branches CH(CH₂)_nCO₂CH₃ as a % of total ester: n≥5 (38.8), n=4

25 (20), n=1,2,3 (15.7), n=0 (25.4).

Example 131

Ethylene and methyl acrylate (20 ml) were copolymerized in 20 ml of CHCl₃ at 50°C for 20 hours according to example 125 using catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆ (0.339 g, 0.40 mmol) to give 0.795 g of copolymer. DSC (two heats, -150 to +150°C, 15°C/min) shows Tg= -48°C.

Example 132

A solution of the ligand (2,6-i-PrPh)₂DAB(Me₂)

(0.045 g, 0.11 mmol) dissolved in 2 ml of CHCl₃ was added to a solution of the complex [PdMe(CH₃CN)(1,5-cyclooctadiene)]+SbF₆- (0.051 g, 0.10 mmol) in 2 ml of CHCl₃. This mixture was combined with 35 ml of

additional CHCl₃ and 5 ml of methyl acrylate in a Schlenk flask in a drybox, and then a copolymerization with ethylene was carried out according to example 125 to give 1.94 g of copolymer.

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Example 133

Methyl acrylate (5 ml) was added to the solid catalyst $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(Et_2O)\}BF_4$ (0.069g, 0.10 mmol) followed by 40 ml of CHCl₃. The addition of methyl acrylate before the CHCl₃ is often important to avoid deactivation of the catalyst. A copolymerization with ethylene was carried out according to example 125 to give 2.87 g of copolymer.

Characterization of poly(ethylene-co-methyl acrylate)

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by 1H NMR

NMR spectra in CDCl₃ were integrated and the polymer compositions and branching ratios were calculated. See example 124 for chemical shifts and assignments.

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Example	Yield(g)	methyl acrylate (mole %)	CH ₃ per 1000 CH ₂	CO ₂ CH ₃ per
124	3.9	6.9	80	42
125	1.75	7.1	104	45
126	4.93	5.6	87	. 34
127	8,19	6.1	87	37
128	1.97	7.3	159	50
129	3.42	9.5	86	59
130	2.17	22.8	29	137
131	0.795	41	14	262
132	1.94	6.1	80 -	36
133	2.87	8.2	70	49

Molecular Weight Characterization

GPC was done in THF using PMMA standards and an RI detector except for example 133 which was done in trichlorobenzene at 135°C vs. polystyrene reference

with results calculated as linear polyethylene using universal calibration theory. When polymer end groups could be detected by ^1H NMR (5.4 ppm, multiplet, - CH=CH-, internal double bond), M_n was calculated assuming two olefinic protons per chain.

Example	Mn	Mw	M_w/M_n	M _n (¹ H NMR)
124	15,500	26,400	1.70	
125	1,540	2,190	1.42	850
126	32,500	49,900	1.54	
127	12,300	22,500	1.83	
128	555	595	1.07	360
129	16,100	24,900	- 1.55	
130	800	3,180	3.98	1,800
131		·		1,100
132	15,200	26,000	1.71	
133	5,010	8,740	1.75	

Example 134

Ethylene and t-butyl acrylate (20 ml) were copolymerized according to example 130 to give 2.039 g 10 of viscous fluid.
¹H NMR of the crude product showed the desired copolymer along with residual unreacted tbutyl acrylate. The weight of polymer corrected for monomer was 1.84 g. The sample was reprecipitated to 15 remove residual monomer by slow addition of excess MeOH to a CHCl3 solution. The reprecipitated polymer was dried in vacuo. 1H NMR (CDCl3): 2.2(t, -CH2CO2C(CH3)3, ester ended branches), 1.6(m, -CH2CH2CO2C(CH3)3, ester ended branches), 1.45(s, -C(CH₃)₃), 0.95-1.45(m, CH and other CH_2), 0.75-0.95(m, CH_3 , ends of hydrocarbon 20 branches or ends of chains). This spectrum shows that the esters are primarily located at the ends of hydrocarbon branches; integration gave 6.7 mole % tbutyl acrylate. 13C NMR quantitative analysis, branching per 1000 CH2: Total methyls (74.8), Methyl 25 (27.7), Ethyl (15.3), Propyl (1.5), Butyl (8.6), ≥Amyl

and end of chains (30.8), $-CO_2C(CH_3)_3$ ester (43.2). Ester branches $-CH(CH_2)_nCO_2C(CH_3)_3$ as a % of total ester: $n\ge 5$ (44.3), n=1,2,3,4 (37.2), n=0 (18.5). GPC (THF, PMMA standard): $M_n=6000$ $M_w=8310$ $M_w/M_n=1.39$.

Example 135

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Glycidyl acrylate was vacuum distilled and inhibited with 50 ppm phenothiazine. Ethylene and glycidyl acrylate (5 ml) were copolymerized according to Example 125 using catalyst {[(2,6-i-

10 PrPh) 2DABMe2 PdCH2CH2CH2C(O)OCH3 SbF6 (0.084 g, 0.10 mmol). The reaction mixture was filtered through a fritted glass filter to remove chloroform insolubles, and the chloroform was removed in vacuo to give 14.1 g viscous yellow oil which still contained residual unreacted glycidyl acrylate. The sample was

unreacted glycidyl acrylate. The sample was reprecipitated to remove residual monomer by slow addition of excess acetone to a CHCl₃ solution. The reprecipitated polymer was dried *in vacuo* to give 9.92 g of copolymer containing 1.8 mole % glycidyl acrylate.

20 ¹H NMR (CDCl₃): 4.4, 3.9, 3.2, 2.85,

n=1,2,3 (50.7), n=0 (9.6).

2.65 (multiplets, 1H each -CH₂CHCH₂O) 2.35 (t,

-CH₂CO₂CH₂CHCH₂O, ester ended branches), 1.65(m,

-CH₂CH₂CO₂CH₂CHCH₂O, ester ended branches), 0.95-1.5(m,CH

and other CH_2), 0.75-0.95(m, CH_3 , ends of hydrocarbon branches or ends of chains). This spectrum shows that the epoxide ring is intact, and that the glycidyl ester groups are primarily located at the ends of hydrocarbon branches. GPC (THF, PMMA standard): $M_n=63,100$ $M_w=179,000$ $M_w/M_n=2.85$.

30 13C NMR quantitative analysis, branching per 1000 CH₂: Total methyls (101.7), Methyl (32.5), Ethyl (21.3), Propyl (2.4), Butyl (9.5), Amyl (1.4), \geq Hexyl and end of chains (29.3), Ester branches -CH(CH₂)_nCO₂R as a % of total ester: n \geq 5 (39.7), n=4 (small amount),

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A 3.24-g sample of the copolymer was dissolved in 50 mL of refluxing methylene chloride. A solution of 0.18 g oxalic acid dihydrate in 5 mL of 1:1 chloroform-acetone was added to the solution of copolymer and the solvent was evaporated off on a hot plate. The thick liquid was allowed to stand in an aluminum pan at room temperature overnight; the pan was then placed in an oven at 70°C for 1.5 hr followed by 110°C/vacuum for 5 hr. The cured polymer was a dark, non-tacky soft rubber which tore easily (it had a very short elongation to break despite its rubberiness).

Example 136

1-Pentene (20 ml) and methyl acrylate (5 ml) were copolymerized in 20 ml chloroform for 96 hours using catalyst $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(0)OCH_3\}SbF_6$ (0.084 g, 0.10 mmol). The solvent and unreacted monomers were removed in vacuo to give 0.303 g copolymer (0.219 g after correcting for catalyst residue). The 1H NMR spectrum was similar to the ethylene/methyl acrylate copolymer of example 124 suggesting that many of the ester groups are located at the ends of hydrocarbon branches. Integration shows that the product contains 21 mole % methyl acrylate. There are 65 acrylates and 96 methyls per 1000 methylene carbons. GPC (THF, PMMA standard): $^1H_1 = 6400$ $^1H_2 = 1100$ $^1H_3 = 1100$ $^1H_4 = 1100$

Example 137

Benzyl acrylate was passed through activity 1 alumina B, inhibited with 50 ppm phenothiazine, and stored over activated 4A molecular sieves. Ethylene and benzyl acrylate (5 ml) were copolymerized according to example 135 to give 11.32 g of viscous fluid. ¹H NMR of the crude product showed a mixture of copolymer and unreacted benzyl acrylate (35 wt %) The residual benzyl acrylate was removed by two reprecitations, the first by addition of excess MeOH to a chloroform solution, and the second by addition of excess acetone to a chloroform solution. ¹H NMR (CDCl₃): 7.35 (broad

s, $-CH_2C_6H_5$), 5.1(s, $-CH_2C_6H_5$), 2.35(t, $-CH_2CO_2CH_2C_6H_5$, ester ended branches), 1.6(m, $-CH_2CH_2CO_2CH_2C_6H_5$, ester ended branches), 0.95-1.5(m, CH and other CH₂), 0.75-0.95(m, CH₃, ends of hydrocarbon branches or ends of chains). Integration shows that the product contains 3.7 mole % benzyl acrylate. There are 21 acrylates and 93 methyls per 1000 methylene carbons. GPC (THF, PMMA standard): M_n =46,200 M_w =73,600 M_w/M_n = 1.59.

13C NMR quantitative analysis, Branching per 1000 CH₂: Total methyls (97.2), Methyl (32.9), Ethyl (20.3), Propyl (2.4), Butyl (9.7), Amyl (2.9), \geq Hexyl and end of chains (35.2), benzyl acrylate (17.9), Ester branches -CH(CH₂)_nCO₂R as a % of total ester: n \geq 5 (44.5), n=4 (7.2), n=1,2,3 (42.3), n=0 (6)

15 Example 138

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1-Pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml chloroform according to example 125 using catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆ (0.084 g, 0.10 mmol) to give 9.11 g highly viscous yellow oil The ¹H

NMR spectrum was similar to the poly(ethylene) of example 110 with 113 methyl carbons per 1000 methylene carbons. ¹³C NMR quantitative analysis, branching per 1000 CH₂: Total methyls (119.5), Methyl (54.7), Ethyl (16.9), Propyl (8.4), Butyl (7.7), Amyl (7.2), ≥Hexyl

and end of chains (30.9). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=25,000$, $M_w=44,900$, $M_w/M_n=1.79$.

Listed below are the ¹³C NMR data upon which the above analysis is based.

	13 _{C NMR Data}		
TCB,	120C, 0.05M CrAcAc		
Freq ppm	Intensity		
39.6012	5.53532		
39.4313	6.33425	MB ₂	
38.3004	8.71403	MB3+	
37.9446	17.7325	MB3+	
37.2809	36.416	αB_1 ,	3B ₃
36.7659	5.10586	αB_1 ,	3B ₃
	226		

34.3181	56.1758	αγ+Β
33.8243	15.6271	αγ+Β
33.3942	8.09189	MB ₁
32.9854	20.3523	MB ₁
32.6721	4.35239	MB ₁
32.327	4.06305	3B ₅
31.9394	27.137	3B ₆ +, 3 EOC
31.4031	9.62823	y+y+B, 3B4
30.235	52.8404	γ+γ+B, 3B ₄
29.7518	162.791	$\gamma + \gamma + B$, $3B_4$
29.3164	26.506	$\gamma + \gamma + B$, $3B_4$
27.5695	15.4471	By+B, 2B2
27.1341	59.1216	Bγ+B, 2B ₂
26.4811	8.58222	By+B, 2B ₂
24.4475	5.93996	ββв
23.12	5.05181	2B ₄
22.6369	29.7047	2B ₅ +, 2 EOC
20.1626	6.29481	2B ₃
19.7378	31.9342	1B ₁
19.2068	3.93019	1B ₁
14.2582	5.59441	· 1B ₃
13.8706	36.3938	1B4+, 1 EOC
10.9768	9.89028	1B ₂
		_

Example 139

1-Pentene (20 ml) was polymerized in 20 ml chloroform according to example 138 to give 2.59 g of viscous fluid (369 equivalents 1-pentene per Pd).

Integration of the ¹H NMR spectrum showed 118 methyl carbons per 1000 methylene carbons. DSC (two heats, -150 to +150°C, 15°C/min) shows Tg= -58°C and a low temperature melting endotherm from

10 -50°C to 30°C (32 J/g).

 ^{13}C NMR quantitative analysis, branching per 1000 CH2: Total methyls (118), Methyl (85.3), Ethyl (none detected), Propyl (15.6), Butyl (non detected), $_{\geq}\text{Amyl}$ and end of chains (17.1). GPC (trichlorobenzene,

15 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=22,500$, $M_w=43,800$, $M_w/M_n=1.94$.

Listed below are the ¹³C NMR data upon which the above analysis is based.

20

 ^{13}C NMR data

	TCB, 120C, 0.05M	CrAcAc
Freq ppm	Intensity	
42.6277	4.69744	αα for Me & Et ⁺
39.5428	9.5323	3 rd carbon of a 6 ⁺ carbon
	·	side chain that has a methyl
		branch at the 4 position
38.1357	3.59535	
37.8384	13.9563	MB ₃ +
37.5888	28.4579	-
37.2224	54.6811	αB_1 , $3B_3$
35.5287	6.51708	
35.2419	3.55603	·
34.6366	7.35366	
34.2437	22.3787	
32.911	45.2064	MB ₁
32.5977	10.5375	_
32.38	4.02878	
31.8809	14.1607	3B ₆ +, 3EOC
30.6916	8.44427	γ ⁺ γ ⁺ Β
30.0703	63.1613	γ ⁺ γ ⁺ Β
29.6987	248	γ+γ+B
29.2633	17.9013	γ+γ+B
28.8916	3.60422	-
27.1182	66.2971	βγ ⁺ Β, (4Β ₅ , etc.)
24.5324	16.8854	-
22.5784	16.0395	2B ₅ +, 2EOC
20.1041	13.2742	
19.6952	54.3903	1B ₁ , 2B ₃
14.2104	12.2831	
13.8281	16.8199	1B ₄ +, EOC, 1B ₃

Integration of the CH₂ peaks due to the structure

5 -CH(R)CH₂CH(R')-, where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 69% of these structures, R = Me. The region integrated for the structure where both R and R' are ≥Ethyl was 39.7 ppm to 41.9 ppm to avoid including an interference from another type of methylene carbon on a side chain.

Example 140

[(2,6-i-PrPh)₂DABMe₂]PdMeCl (0.020 g, 0.036 mmol) was dissolved in 4 ml CH₂Cl₂ and methyl acrylate (0.162 g, 0.38 mmol, inhibited with 50 ppm phenothiazine) was added while stirring. This solution was added to a stirred suspension of NaBAF (0.033 g, 0.038 mmol) in 4 ml of CH₂Cl₂. After stirring for 1

cour, the mixture was filtered through a 0.5 μm PTFE
membrane filter to remove a flocculant gray
precipitate. The solvent was removed from the filtrate
in vacuo to give a solid which was recrystallized from
a CH2Cl2/pentane mixture at -40°C to give 0.39 g (75%
yield) of orange crystalline {[(2,6-i-PrPh)2DABMe2]PdCH2CH2CH2C(0)OCH3}BAF. 1H NMR (CDCl3):
0.65(m, CH2, 2H); 1.15-1.45(four sets of doublets for
-CH(CH3)2 and multiplet at 1.4 for a CH2, total area =
26H); 2.19,2.21 (s,s, CH3 of ligand backbone, 6H);
2.40(m, CH2, 2H); 2.90 (m, -CH(CH3)2, 4H); 3.05(s, -CO2CH3, 3H); 7.25-7.75(m, aromatic H of ligand and counterion, 19H).

All GPC data reported for examples 141-170, 177, and 204-212 were run in trichlorobenzene vs. polyethylene standards unless otherwise indicated. All DSC data reported for examples 141-170, 177, and 204-212 (second heat, -150°C to 150°, 10 or 15°C/min).

Example 141

A Schlenk flask containing {[(2,6-i-20 PrPh) $_2DABH_2$] NiMe (Et $_2O$) $_3BAF^-$ (1.3 mg, 8.3 x $_3D^{-7}$ mol) under an argon atmosphere was cooled to -78°C. cooling, the argon was evacuated and the flask backfilled with ethylene (1 atm). Toluene (75 mL) was added via syringe. The polymerization mixture was then 25 warmed to 0°C. The solution was stirred for 30 minutes Polymer began to precipitate from the solution within minutes. After 30 minutes, the polymerization was terminated upon exposing the catalyst to air. The polymer was precipitated from acetone, collected by 30 filtration and washed with 6 M HCl, water, and acetone. The polymer was dried in vacuo. The polymerization yielded 1.53 g of polyethylene (1.3 x 10^5 TO). M_n = 91,900; $M_w = 279,000$; $M_w/M_n = 3.03$; $T_m = 129$ °C. ¹H NMR $(C_6D_5C1, 142^{\circ}C)$ 0.6 methyls per 100 carbons. 35

Example 142

The reaction was done in the same way as in Example 141 using 1.3 mg of $\{[(2,6-i-$

 $^{-1}$ rPh)₂DABMe₂ $^{-1}$ NiMe(Et₂O) $^{-1}$ BAF (8.3 x 10⁻⁷ mol). The polymer was isolated as a white solid (0.1 g).

Examples 143-148

General procedure for the polymerization of 5 ethylene by the methylaluminoxane (MAO) activation of nickel complexes containing bidentate diimine ligands: Polymerization at 0°C: The bisimine nickel dihalide complex $(1.7 \times 10^{-5} \text{ mol})$ was combined with toluene (100 mL) in a flame dried Schlenk flask under 1 atmosphere 10 ethylene pressure. The polymerization was cooled to 0°C in an ice-water bath. The mixture was stirred at 0°C for 15 minutes prior to activation with MAO. Subsequently, 1.5 mL of a 10% MAO (100 eq) solution in toluene was added onto the nickel dihalide suspension. 15 The solution was stirred at 0°C for 10, 30, or 60 minutes. Within minutes increased viscosity and/or precipitation of polyethylene was observed. polymerization was quenched and the polymer precipitated from acetone. The polymer was collected by suction filtration and dried under vacuum for 24 20 See Table I for a detailed description of molecular weight and catalyst activity data.

	Example No.	Catalyst
	143	[(2,6-i-PrPh)2DABH2]NiBr2
25 .	144	[(2,6-i-PrPh)2DABMe2]NiBr2
	145	[(2,6-MePh)2DABH2]NiBr2
	146	[(2,6-i-PrPh)2DABAn]NiBr2
	147	[(2,6-MePh) ₂ DABAn]NiBr ₂
	148	[(2,6-MePh)2DABMe2]NiBr2

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Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	Mn	Mw	M _w /M _n	Thermal Analysis
143	0°C. 30 m	5.3	22,700	80,900	231,000	2.85	119 (T _m)
1442	0°C. 30 m	3.8	16,300	403,000	795,000	1.97	115 (T _m)
1453	0°C. 30 m	3.4	14,300	42,900	107,000	2.49	131 (T _m)
1462	0°C. 30 m	. 7.0	29,900	168,000	389,000	2.31	107 (T _m)
147	0°C .10 m	3.7	47,500	125,000	362,000	2.89	122 (T _m)
148	0°C, 10 m	5.1	65,400	171,000	440,000	2.58	115 (T _m)

- 1 Polymerization reactions run at 1 atmosphere
 ethylene pressure.
 - ² Branching Analysis by ¹³C NMR per 1000 CH₂:
 - Ex. 144: Total methyls (54.3), Methyl (43.4),
- 5 Ethyl (3.3), Propyl (2), Butyl (1.3), ≥Butyl and end of chains (5.7).
 - Ex. 146: Total methyls (90.9), Methyl (65.3), Ethyl (7.2), Propyl (4.5), Butyl (3.5), Amyl (4.5), \geq Hexyl and end of chains (10.2).
- 3 Ex. 145: $^{.1}\text{H}$ NMR (C₆D₅Cl), 142°C) 0.1 methyl per 100 carbon atoms.

Examples 149-154

Polymerization at Ambient Temperature

The general procedure described for the MAO

15 activation of the diimine nickel dihalides was followed in the polymerizations detailed below, except all polymerizations were run between 25-30°C.

	<u>Example No.</u>	<u>Catalyst</u>
20	149	[(2,6-i-PrPh) ₂ DABH ₂]NiBr ₂
	150	[(2,6-i-PrPh) ₂ DABMe ₂]NiBr ₂
	151	[(2,6-MePh)2DABH2]NiBr2
	152	$[(2,6-i-PrPh)_2DABAn]NiBr_2$
	153	[(2,6-MePh) ₂ DABAn]NiBr ₂
25	154	[(2,6-MePh)2DABMe2]NiBr2

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	Mn	M _W	M _w /M _n	Thermal Analysis (°C)
149	30°C, 30 m	2.5	12,200	15,500	34,900	2.25	- -
1504	25°C, 30 m	3.4	14,500	173,000	248,000	1.44	-51 (T _g)
1513	25°C. 30 m	7.2	30,800	13,900	39,900	2.88	90,112 (T _m)
1524	25°C. 30 m	4.2	18,000	82,300	175,000	2.80	39 (T _m)
153	25°C .10 m	4.9	62,900	14,000	25,800	1.85	
154	25°C, 10 m	3.7	47,500	20,000	36,000	1.83	

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- Polymerization reactions run at 1 atmosphere ethylene pressure.
 - ² Branching Analysis by ¹³C NMR per 1000 CH₂:

Ex. 150: Total methyls (116.3), Methyl (93.5),

5 Ethyl (6.2), Propyl (3.2), Butyl (2.9), Am (6.6), ≥Hex and end of chains (11.2).

Ex. 152: Total methyls (141.9), Methyl (98.1), Ethyl (15.9), Propyl (5.6), Butyl (6.8), Amyl (4.1), \geq Hex and end of chains (10.7). Quantitation of the - CH₂CH(CH₃)CH₂CH₃ structure per 1000 CH₂'s: 8.

 3 Ex. 151: 1H NMR (C₆D₅Cl), 142°C) 3 methyl per 100 carbon atoms.

Example 155

A standard solution of [(2,6-i-PrPh)₂DABAn]NiBr₂
was prepared as follows: 1,2-difluorobenzene (10 mL)
was added to 6.0 mg of [(2,6-i-PrPh)₂DABAn]NiBr₂ (8.4 x
10⁻⁶ mol) in a 10 mL volumetric flask. The standard
solution was transferred to a Kontes flask and stored
under an argon atmosphere.

The standard catalyst solution (1.0 mL, 8.4 x 10⁻⁷ mol catalyst) was added to a Schlenk flask which contained 100 mL toluene, and was under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 1.5 mL of a 10% solution of MAO (≥1000 eq) was added.

The solution was stirred for 30 minutes. Polymer began to precipitate within minutes. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried in vacuo (2.15 g, 1.84 x 10^5 TO). $M_n=489,000;\ M_w=1,200,000;\ M_w/M_n=2.47$

Example 156

The polymerization of ethylene at 25°C was accomplished in an identical manner to that described in Example 155. The polymerization yielded 1.8 g of polyethylene (1.53 x 10^5 TO). $M_n = 190,000$; $M_w = 410,000$; $M_w/M_n = 2.16$; ¹H NMR (C₆D₅Cl, 142°C) 7 methyls per 100 carbons.

Example 157

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A standard solution of $[(2,6-\text{MePh})_2\text{DABAn}]\text{NiBr}_2$ was prepared in the same way as described for the complex in Example 155 using 5.0 mg of $[(2,6-\text{MePh})_2\text{DABAn}]\text{NiBr}_2$ (8.4 x 10⁻⁶ mol).

Toluene (100 mL) and 1.0 mL of the standard solution of complex 5 (8.3 x 10^{-7} mol catalyst) were combined in a Schlenk flask under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 1.5 mL of a 10% solution of MAO(\geq 1000 eq) was added. The polymerization mixture was stirred for 30 minutes. The polymerization was terminated and the polymer precipitated from acetone. The reaction yielded 1.60 g of polyethylene (1.4 x 10^5 TO). Mn = 590,000; Mw = 1,350,000; Mw/Mn = 2.29.

15 Example 158

Toluene (200 mL) and 1.0 mL of a standard solution of [(2,6-i-PrPh)₂DABAn]NiBr₂ (8.3 x 10^{-7} mol catalyst) were combined in a Fisher-Porter pressure vessel. The resulting solution was cooled to 0°C, and 1.0 mL of a 10% MAO (\geq 1000 eq) solution in toluene was added to activate the polymerization. Subsequent to the MAO addition, the reactor was rapidly pressurized to 276 kPa. The solution was stirred for 30 minutes at 0°C. After 30 minutes, the reaction was quenched and polymer precipitated from acetone. The resulting polymer was dried under reduced pressure. The polymerization yielded 2.13 g of white polyethylene (1.82 x 10^5 TO). $M_{\rm n}$ = 611,000; $M_{\rm w}$ = 1,400,000; $M_{\rm w}/M_{\rm n}$ = 2.29; $T_{\rm m}$ = 123°C; 1 H NMR (1 C6D₅C1, 142°C) 0.5 methyls per 100 carbons.

Examples 159-160

Polymerization of Propylene

The diimine nickel dihalide complex (1.7x10⁻⁵ mol) was combined with toluene (100 mL) in a Schlenk flask under 1 atmosphere propylene pressure. The polymerization was cooled to 0°C, and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The solution was stirred for 2 hours. The polymerization

tas quenched and the polymer precipitated from acetone. The polymer was dried under vacuum.

Example No.

Catalyst

159

[(2,6-i-PrPh)2DABH2]NiBr2

5 160

[(2,6-i-PrPh)₂DABAn]NiBr₂

Exam.	Condi-	Yield	TO/	Mn	Mw	$M_{\rm w}/M_{\rm n}$	Thermal
	tions ¹	(g)	hr·mol				Analysis
			catalyst				(°C)
159	0°C. 2 h	1.3	900	131,000 a	226,000	1.72	-20 (Tg)
160	0°C. 2 h	4.3	2,900	147,000	235,000	1.60	-78, -20 (T _q)

aGPC (toluene, polystyrene standard)

Ex. 159: ^{1}H NMR (C₆D₅Cl); 142°C) 30 methyls per 100 carbon atoms.

10 Ex. 160: ¹H NMR (C_6D_5Cl), 142°C) 29 methyls per 100 carbon atoms. Quantitative ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (699). Based on the total methyls, the fraction of 1,3-enchainment is 13%. Analysis of backbone carbons (per 1000 CH₂): δ^+ (53), 15 δ^+/γ (0.98).

Listed below are the ¹³C NMR data upon which the above analysis is based.

20

13C NMR Data
TCB, 140C, 0.05M CrAcAc

	TCB,	140C, 0.05M	CrA	CAC		
Freq ppm		Intensity				
 47.3161		53.1767				
46.9816		89.3849				
46.4188		82.4488				
45.84		23.1784				
38.4702		12.8395				
38.0985		29.2643				
37.472		18.6544				
37.2915		24.8559		,		
35.3747		15.6971				
34.5623		14.6353				
33.3145		14.2876				-
32.996		12.2454				
30.9464		24.2132				
30.6703		57.4826				
30.081		30.122	γ	to	single	branch

234

29.6987	29.2186	δ^+ to branch
28.3659	298.691	
27.4792	33.2539	·
27.1235	29.7384	
24.5324	9.45408	
21.1554	20.0541	
20.6244	110.077	
19.9926	135.356	
16.9342	8.67216	
16.4829	8.81404	
14.9962	8.38097	

Example 161

 $[(2,6-i-PrPh)_2DABH_2]NiBr_2 \ (10 \text{ mg},\ 1.7 \times 10^{-5} \text{ mol})$ was combined with toluene (40 mL) under a N_2 atmosphere. A 10% solution of MAO (1.5 mL, 100 eq) was added to the solution. After 30 minutes, the Schlenk flask was backfilled with propylene. The reaction was stirred at room temperature for 5.5 hours. The polymerization was quenched, and the resulting polymer dried under vacuum (670 mg, 213 TO/h). $M_n = 176,000;$ $M_w = 299,000; M_w/M_n = 1.70.$ Quantitative ^{13}C NMR analysis, branching per 1000 CH₂: Total methyls (626), Methyl (501), Ethyl (1), \geq Butyl and end of chain (7). Based on the total methyls, the fraction of 1,3-enchainment is 22%. Analysis of backbone carbons (per 1000 CH₂): δ + (31), δ +/ γ (0.76).

Examples 162-165

The diimine nickel dihalide catalyst precursor (1.7x10⁻⁵ mol) was combined with toluene (40 mL) and 1-hexene (10 mL) under a N₂ atmosphere. Polymerization reactions of 1-hexene were run at both 0°C and room temperature. A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. Typically the polymerization reactions were stirred for 1-2 hours. The polymer was precipitated from acetone and collected by suction filtration. The resulting polymer was dried under vacuum.

	Ex. No.	Catalyst
	162	[(2,6-i-PrPh)2DABH2]NiBr2
	163	[(2,6-i-PrPh) ₂ DABAn]NiBr ₂
	164	[(2,6-i-PrPh)2DABH2]NiBr2
5	165	[(2,6-i-PrPh),DABAn]NiBr

Exam.	Condi- tions ¹	Yield (g)	TO/ hr·mol catalyst	_{Мп} а	M _w	M _w /M _n	Thermal Analysis (°C)
162	25°C. 1 h	3.0	2100	173,000	318,000	1.84	-48 (T _q)
163	25°C, I h	1.2	860	314,000	642,000	2.05	-54 (Tg)
164	0°C, 2 h	3.0	1100	70,800	128,000	1.80	-45 (T _q)
165	0°C. 2 h	1.5	540	91,700	142,000	1.55	-49 (T _q)

aGPC (toluene, polystyrene standards).

Branching Analysis Ex. 162: by ^{13}C NMR per 1000 $^{\circ}$ CH₂:

10 Total methyls (157.2), Methyl (47), Ethyl (1.9), Propyl (4.5), Butyl (101.7), ≥Am and end of chain (4.3).

13C NMR data (Example 162)

TCB, 120C, 0.05M CrAcAc

	TCB, 120C, 0.05M C1	racac
Freq ppm	Intensity	
42.8364	7.99519	Methine
41.3129	27.5914	αα to two Eth+ branches
40.5759	19.6201	αα to two Eth+ branches
37.8831	14.7864	Methines and Methylenes
37.2984	93.6984	Methines and Methylenes
36,6684	6.99225	Methines and Methylenes
35.5773	36.067	Methines and Methylenes
34.655	55.825	Methines and Methylenes
34.3091	63.3862	Methines and Methylenes
33.8356	24.1992	Methines and Methylenes
33.428	53.7439	Methines and Methylenes
32.9957	51.1648	Methines and Methylenes
31.9169	17.4373	Methines and Methylenes
31.5546	14.008	Methines and Methylenes
31.1552	10.6667	Methines and Methylenes
30.5993	34.6931	Methines and Methylenes
30.274	56.8489	Methines and Methylenes
30.1258	42.1332	Methines and Methylenes
29.747	97.9715	Methines and Methylenes
29.1047	47.1924	Methines and Methylenes
28.8823	64.5807	Methines and Methylenes
28.1289	13.6645	Methines and Methylenes
27.5648	61.3977	Methines and Methylenes
27.1777	50.9087	Methines and Methylenes
27.0213	31.6159	Methines and Methylenes
26.9142	31.9306	Methines and Methylenes
26.4572	4.715666	Methines and Methylenes
23.2085	154.844	2B ₄
22.6074	12.0719	2B ₅ +, EOC
20.0669	8.41495	1B ₁
19.6963	57.6935	1B ₁
15.9494	17.7108	
14.3477	8.98123	•
13.8742	248	1B ₄ +, EOC

Example 166

[(2,6-i-PrPh)₂DABMe₂]NiBr₂ (10.4 mg, 1.7 x 10⁻⁵ mol) was combined with toluene (15 mL) and 1-hexene (40 mL) under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO (100 eq) solution in toluene was added. The reaction was stirred at 0°C for 2.5 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (1.4g). Mn = 299,000; Mw = 632,000; Mw/Mn = 2.12.

Branching Analysis by 13 C NMR per 1000 CH₂: Total methyls (101.3), Methyl (36.3), Ethyl (1.3), Propyl (6.8), Butyl (47.7), \geq Amyl and end of chains (11.5).

Example 167

 $[(2,6-i-PrPh)_2DABH_2]NiBr_2$ (10 mg, 1.7 x 10⁻⁵ mol) was added to a solution which contained toluene (30 mL) and 1-octene (20 mL) under 1 atm ethylene. A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. The resulting purple solution was allowed to stir for 4 hours at room temperature. Solution viscosity increased over the duration of the polymerization. The polymer was precipitated from acetone and dried under vacuum resulting in 5.3 g of copolymer. $M_n = 15,200$, $M_w = 29,100$, $M_n/M_w = 1.92$.

Example 168

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35

[(2,6-i-PrPh)₂DABAn]NiBr₂ (12 mg, 1.7x10⁻⁵ mol) was combined with toluene (75 mL) in a Schlenk flask under 1 atmosphere ethylene pressure. The mixture was cooled to 0°C, and 0.09 mL of a 1.8 M solution in toluene of Et₂AlCl (10 eq) was added. The resulting purple solution was stirred for 30 minutes at 0°C. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (6.6 g, 2.8 x 10⁴ TO). M_n 25 = 105,000; M_w = 232,000; M_w/M_n = 2.21

Example 169

 $[(2,6-i-PrPh)_2DABAn]NiBr_2$ (12 mg, $1.7x10^{-5}$ mol) was combined with toluene (75 mL) under 1 atmosphere propylene pressure. The solution was cooled to 0°C and 0.1 mL of Et₂AlCl (\geq 10 eq) was added. The reaction was stirred at 0°C for 2 hours. The polymerization was quenched and the polymer precipitated from acetone. The resulting polymer was dried under reduced pressure (3.97 g, 2800 TO).

Example 170

 $\label{eq:combined} $\{(2,6-i-PrPh)_2DABAn\}$ NiBr_2 (12 mg, 1.7x10^{-5} mol)$ was combined with toluene (50 mL) and 1-hexene (25 mL) under a N_2 atmosphere. Et_2AlCl (0.01 mL, 10 eq) was$

added to the polymerization mixture. The resulting purple solution was allowed to stir for 4 hours. After 4 hours the polymerization was quenched and the polymer precipitated from acetone. The polymerization yielded 1.95 g poly(1-hexene) (348 TO/h). $M_n = 373,000$; $M_w = 680,000$; $M_w/M_n = 1.81$.

Example 171

1-Tetradecene (20 ml) was polymerized in methylene chloride (10 ml) for 20 hr using catalyst {[(2,6-i- $PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}SbF_6$ (0.04 g, 0.05 10 mmol). The solvent and reacted monomer were removed in The polymer was precipitated to remove unreacted monomer, by the addition of acetone to a chloroform solution. The precipitated polymer was dried in vacuo to give a 10.2 g yield. 13C NMR 15 (trichlorobenzene, 120°C) integrated to give the following branching analysis per 1000 methylene carbons: Total methyls (69.9), methyl (24.5), ethyl (11.4), propyl (3.7), butyl (2.3) amyl (0.3), ≥Hexyl and end of chain (24.2). Thermal analysis showed Tg = 20 -42.7° C, and Tm = 33.7°C (15.2 J/g).

Listed below are the ¹³C NMR data upon which the above analysis is based.

13_{C NMR Data}

TCR	1200	0.05M	CrAcAc
105,	1200,	0.0314	CIACAC

	100, 1100, 0	. Con Circon
 Freq ppm	Intensity	
39.3416	7.78511	MB ₂
38.2329	5.03571	MB3+
37.8616	9.01667	MB ₃ +
37.5857	3.33517	MB ₃ +
37.2462	31.8174	αB_1 , $3B_3$
36.6415	2.92585	αB_1 , $3B_3$
34.668	5.10337	αγ ⁺ B
34.2384	38.7927	αγ ⁺ B
33.7397	16.9614	3B ₅
33.3471	3.23743	3B ₆ +, 3EOC
32.9387	16.0951	$\gamma^+\gamma^+B$, $3B_4$
31.9148	27.6457	γ ⁺ γ ⁺ Β, 3Β ₄
31.1297	6.03301	γ ⁺ γ ⁺ Β, 3Β ₄
30.212	59.4286	γ ⁺ γ ⁺ Β, 3Β ₄
29.7398	317.201	γ+γ+B, 3B ₄
29.310Í	32.1392	$\gamma^+\gamma^+B$, $3B_4$
27.1511	46.0554	$\beta \gamma^{+}B$, $2B_2$
27.0185	53.103	$\beta \gamma^{+} B$, $2B_{2}$
26.419	9.8189	$\beta \gamma^{+}B$, $2B_{2}$
24.244	2.46963	ββв
22.6207	28.924	2B ₅ +, 2EOC
20.0479	3.22712	2B ₃
19.7084	18.5679	1B ₁
14.3929	3.44368	1B3
13.8677	30.6056	1B ₄ +, 1EOC
10.9448	9.43801	1B ₂

Example 172

4-Methyl-1-pentene (20 ml) was polymerized in methylene chloride (10 ml) for 19 hr using catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(0)OCH₃}SbF₆ (0.04 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to remove residual monomer by addition of excess acetone to a chloroform solution. The precipitated polymer was dried in vacuo to give a 5.7 g yield. ¹³C NMR (trichlorobenzene, 120°C) integrated to give 518 methyls per 1000 methylene carbon atoms. Thermal analysis showed Tg -30.3°C.

Listed below are the ¹³C NMR data upon which the above analysis is based.

13C NMR Data
TCB, 120C, 0.05M CrAcAc

TCB,	120C, 0.05M CFACAC
Freq ppm	Intensity
47.8896	13.3323
47.4011	8.54293
45.7127	26.142
45.1392	17.4909
43.9658	13.9892
43.1375	12.7089
42.6171	11.5396
41.8207	9.00437
39.203	64.9357
37.9712	24.4318
37.3075	87.438
35.4862	16.3581
34.9553	24.5286
34.35	31.8827
33.3624	25.7696
33.0226	42.2982
31.4403	25.3221
30.6226	38.7083
28.504	_. 26.8149
27.989	81.8147
27.7341	78.3801
27.5802	94.6195
27.458	75.8356
27.0864	35.5524
25.6103	97.0113
23.4333	59.6829
23.0563	41.5712
22.536	154.144
21.9944	5.33517
20.7307	16.294
20.4971	34.7892
20.2953	29.9359
19.7378	62.0082

Example 173

1-Eicosene (19.0 g) was polymerized in methylene chloride (15 ml) for 24 hr using catalyst {[(2,6-i-PrPh)2DABMe2]PdCH2CH2CH2C(0)OCH3}SbF6 (0.047 g, 0.05 mmol). The solvent and unreacted monomer were removed in vacuo. The polymer was precipitated to remove residual monomer by addition of excess acetone to a chloroform solution of the polymer. The solution was filtered to collect the polymer. The precipitated polymer was dried in vacuo to give a 5.0 g yield. ¹³C NMR quantitative analysis, branching per 1000 CH2: Total methyls (27), Methyl (14.3), Ethyl (0), Propyl

(0.2), Butyl (0.6), Amyl (0.4), \geq Hexyl and end of chains (12.4).

Integration of the CH_2 peaks due to the structure $-CH(R)CH_2CH(R')$, where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 82% of these structures, R = Me.

Listed below are the ¹³C NMR data upon which the above analysis is based.

10

¹³C NMR data

	TCB, 120C, 0.05M	Cracac
Freg ppm	Intensity	
37.7853	13.978	MB ₂ +
37.1428	52.1332	αΒ
34.1588	41.067	αB ₄ +
32.826	26.670 7 .	MB ₁
31.8066	24. 9262	3B ₆ +, 3EOC
30.0703	96.4154	γ+γ+B, 3B ₄
29.6243	1239.8	γ+γ+B, 3B ₄
27.0013	78.7094	$B\gamma^+B$, $(4B_5$, etc.)
22.5041	23.2209	2B5+, 2EOC
19.605	30.1221	1B ₁
13.759	23.5115	1B ₄ +, EOC

Example 174

The complex [(2,6-i-PrPh)₂DABH₂]PdMeCl (0.010 15 g, 0.019 mmol) and norbornene (0.882 g, 9.37 mmol) were weighed into a vial and dissolved in 2 ml CH2Cl2. NaBAF (0.032g, 0.036 mmol) was rinsed into the stirring mixture with 2 ml of CH2Cl2 After stirring about 5 minutes, there was sudden formation of a solid 20 precipitate. Four ml of o-dichlorobenzene was added and the solution became homogenous and slightly viscous. After stirring for 3 days, the homogeneous orange solution was moderately viscous. The polymer was precipitated by addition of the solution to excess 25 MeOH, isolated by filtration, and dried in vacuo to give 0.285 g (160 equivalents norbornene per Pd) bright orange glassy solid. DSC (two heats, 15°C/min) showed no thermal events from -50 to 300°C. This is consistent with addition type poly(norbornene). Ringopening polymerization of norbornene is known to 30

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produce an amorphous polymer with a glass transition temperature of about 30-55°C.

Example 175

The solid complex {[(2,6-i-

PrPh),DABH,]PdMe(Et,O)}SbF, (0.080 g, 0.10 mmol) was added as a solid to a stirring solution of norbornene (1.865 g) in 20 ml of o-dichlorobenzene in the drybox. About 30 min after the start of the reaction, there was slight viscosity (foam on shaking) and the homogeneous mixture was dark orange/red. After stirring for 20 h, 10 the solvent and unreacted norbornene were removed in vacuo to give 0.508 g orange-red glassy solid (54 equivalents norbornene/Pd). 1H NMR (CDCl3): broad featureless peaks from 0.8-2.4 ppm, no peaks in the olefinic region. This spectrum is consistent with 15 addition type poly(norbornene). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): Mn=566 Mw=1640 Mw/Mn=2.90.

20 Example 176

4-Methyl-1-pentene (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of chloroform according to example 125 using catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(0)OCH₃}SbF₆ (0.084 g, 0.10 mmol) to give 23.29 g highly viscous yellow oil. The ¹H NMR spectrum was similar to the poly(ethylene) of example 110 with 117 methyl carbons per 1000 methylene carbons. ¹³C NMR quantitative analysis, branching per 1000 CH₂: Total methyls (117.1), Methyl (41.5), Ethyl (22.7), Propyl (3.3), Butyl (13), Amyl (1.2), ≥Hexyl and end of chains (33.1), ≥Amyl and end of chains (42.3), By ¹³C NMR this sample contains two identifiable branches at low levels attributable to 4-methyl-1-pentene. The Bu and ≥Amyl peaks contain small contributions from isopropyl ended branch structures.

Example 177

 $CoCl_2$ (500 mg, 3.85 mmol) and (2,6-i-PrPh) DABAn (2.0 g, 4.0 mmol) were combined as solids and dissolved

in 50 mL of THF. The brown solution was stirred for 4 hours at 25°C. The solvent was removed under reduced pressure resulting in a brown solid (1.97 g, 82% yield).

immediately transferred to another Schlenk flask and dissolved in 50 mL of toluene under 1 atmosphere of ethylene. The solution was cooled to 0°C, and 1.5 mL of a 10% MAO solution in toluene was added. The resulting purple solution was warmed to 25°C and stirred for 12 hours. The polymerization was quenched and the polymer precipitated from acetone. The white polymer (200 mg) was collected by filtration and dried under reduced pressure. Mn = 225,000, Mw = 519,000, Mw/Mn = 2.31, Tg = -42°, Tm = 52°C and 99.7°C.

Example 178

Ethyl 10-undecenoate (10 ml) and ethylene (1 atm) were copolymerized in 30 ml of CH_2Cl_2 according to example 125 using catalyst {[(2,6-i-

- 20 PrPh)₂DABMe₂] PdCH₂CH₂C(O)OCH₃}SbF₆ (0.084 g, 0.10 mmol). The copolymer was precipitated by removing most of the CH₂Cl₂ in vacuo, followed by addition of excess acetone. The solution was decanted and the copolymer was dried in vacuo to give 1.35 g viscous fluid. ¹H
- 25 NMR (CDCl₃): 0.75-0.95(m, CH₃); 0.95-1.5(m, C(0)OCH₂CH₃, CH₂, CH); 1.5-1.7(m, -CH₂CH₂C(0)OCH₂CH₃);
 1.9-2.0(m, -CH₂CH=CH-); 2.3(t, -CH₂CH₂C(0)OCH₂CH₃);
 4.15(q, -CH₂CH₂C(0)OCH₂CH₃); 5.40(m, -CH=CH-). The
 olefinic and allylic peaks are due to isomerized ethyl
- 10-undecenoate which has coprecipitated with the copolymer. Adjusting for this, the actual weight of copolymer in this sample is 1.18 g. The copolymer was reprecipitated by addition of excess acetone to a chloroform solution. ¹H NMR of the reprecipitated
- polymer is similar except there are no peaks due to isomerized ethyl 10-undecenoate at 1.9-2.0 and 5.40 ppm. Based on integration, the reprecipitated copolymer contains 7.4 mole % ethyl 10-undecenoate, and

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7.3 methyl carbons per 1000 methylene carbons. 13 C NMR quantitative analysis, branching per 1000 CH²: Total methyls (84.5), Methyl (31.7), Ethyl(16.9), Propyl (1.5), Butyl (7.8), Amyl (4.4), \geq Hexyl and end of chains (22.3). GPC (THF, PMMA standard): Mn=20,300 Mw=26,300 Mw/Mn = 1.30. 13 C NMR quantitative analysis, branching per 1000 CH2: ethyl ester (37.8), Ester branches -CH(CH₂)nCO₂CH₂CH₃ as a % of total ester: n \geq 5 (65.8), n=4 (6.5), n=1,2,3 (26.5), n=0 10 (1.2).

Listed below are the ¹³C NMR data upon which the above analysis is based.

13C NMR Data

	TOC NMR Data
Freq ppm	Intensity
59.5337	53.217
39.7234	2.57361
39.3145	7.80953
38.2207	11.9395
37.8437	20.3066
37.2225	29.7808
36.7181	5.22075
34.6792	17.6322
34.265	107.55
33.7181	21.9369
33.3093	8.22574
32.9164	15.0995
32.396	8.52655
32.0828	5.79098
31.9075	37.468
31.127	13.8003
30.6757	8.38026
30.2084	52.5908
29.9961	27.3761
29.72	151.164
29.5076	39.2815
29.2899	69.7714
28.727	6.50082
27.5164	20.4174
26.9908 26.5713	64.4298
26.3749	9.18236 11.8136
25.5519	4.52152
25.0528	43.7554
24.2457	7.9589
23.1094	10.0537
22.9926	4.71618
22.6156	37.2966
20.0245	2.4263
19.6847	25.9312
19.1643	5.33693
17.5183	2.20778
14.2954	66.1759
13.8653	43.8215
13.414	2.52882
11.1521	, 5 . 9183
10.9237	14.9294
174.945	3.27848
172.184	125.486
171.695	4.57235

Example 179

The solid complex {[(2,6-i-

 $PrPh)_2DABH_2]PdMe(Et_2O)\}SbF_6$ (0.080 g, 0.10 mmol) was added as a solid to a stirring solution of cyclopentene (1.35 g, 20 mmol) in 20 ml of dichlorobenzene in the

drybox. After stirring 20 h, the slightly viscous solution was worked up by removing the solvent in vacuo to give 1.05 g sticky solid (156 equivalents of cyclopentene per Pd). 1H NMR (CDCl3): complex spectrum 5 from 0.6-2.6 ppm with maxima at 0.75, 1.05, 1.20, 1.55, 1.65, 1.85, 2.10, 2.25, and 2.50. There is also a multiplet for internal olefin at 5.25-5.35. consistent with a trisubstituted cyclopentenyl end group with a single proton (W. M. Kelly et. al., Macromolecules 1994, 27, 4477-4485.) Integration 10 assuming one olefinic proton per polymer chain gives DP=8.0 and Mn=540. IR (Thin film between NaCl plates, cm⁻¹): 3048 (vw, olefinic end group, CH stretch), 1646 (vw, olefinic end group, R2C=CHR trisubstituted double bond stretch), 1464(vs), 1447(vs), 1364(m), 15 1332(m), 1257(w), 1035(w), 946(m), 895(w), 882(w), 803 (m, cyclopentenyl end group, R2C=CHR trisubstituted double bond, CH bend), 721 (vw, cyclopentenyl end group, RHC=CHR disubstituted double bond, CH bend). (trichlorobenzene, 135°C, polystyrene reference, 20 results calculated as linear polyethylene using universal calibration theory): $M_n=138$ $M_w=246$ $M_{\rm W}/M_{\rm n}=1.79$.

Example 180

The solid complex {[(2,6-i-25 PrPh) 2DABMe2 PdCH2CH2CH2C(0)OCH3 SbF6 (0.084 g, 0.10 mmol) was added to a stirring solution of 10.0 ml cyclopentene in 10 ml CHCl3 in the drybox. After stirring for 20 h, the mixture appeared to be separated into two phases. The solvent and unreacted monomer 30 were removed in vacuo leaving 2.20 g off-white solid (323 equivalents cyclopentene per Pd). DSC (25 to 300°C, 15°C/min, first heat): Tg = 107°C, Tm (onset) = 165 °C, Tm (end) = 260 °C, Heat of fusion = 29 J/g. Similar results were obtained on the second heat. 35 GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using

iniversal calibration theory): $M_n=28,700$ $M_w=33,300$ $M_w/M_n=1.16$.

Listed below are the ¹³C NMR analysis for this polymer.

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13C NMR Data
TCB, 120C, 0.05M CrAcAc

ICB,	120C, U.USM CIACAC
Freq ppm	Intensity
46.4873	142.424
38.339	59.7617
30.5886	137.551

Example 181

The solid complex {[(2,6-i-

 $PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}SbF_6$ (0.084 g, 0.10 10 mmol) was added to a stirring solution of 10.0 ml cyclopentene in 10 ml CHCl3 in a Schlenk flask. flask was evacuated briefly and refilled with ethylene. It was maintained under slightly above 1 atm ethylene pressure using a mercury bubbler. After 20 h, the 15 solvent and unreacted monomers were removed in vacuo from the homogeneous solution to give 12.89 g of highly viscous fluid. ¹H- NMR (CDCl₃): cyclopentene peaks: 0.65(m, 1H); 1.15(broad s, 2H); 1.5-2.0(m, 5H); ethylene peaks: 0.75-0.95(m, CH₃); 0.95-1.5(m, CH and 20 CH2). Integration shows 24 mole % cyclopentene in this copolymer. Analysis of the polyethylene part of the spectrum (omitting peaks due to cyclopentyl units) shows 75 total methyl carbons per 1000 methylene carbons. Based on quantitative 13C analysis, the 25 distribution of branches per 1000 methylene carbons is Methyl (21), Ethyl (13), Propyl (\sim 0), Butyl (20) and \geq Amyl (20). DSC (first heat: 25 to 150°C, 10°C/min; first cool: 150 to -150°C, 10°C/min; second heat: -150 to 150°C, 10°C/min,; values of second heat reported): $Tq = -33 \,^{\circ}C$, $Tm = 19 \,^{\circ}C$ (11 J/g). GPC (trichlorobenzene, 30 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory): $M_n=3,960$ $M_w=10,800$ $M_w/M_n=2.73$.

Listed below are the $^{13}\mathrm{C}$ NMR data upon which the above analysis is based.

13_{C NMR Data}

TCB, 120C, 0.05M CrAcAc

		ICB,	120C, U.USM CIACAC
	Freq ppm	Intensity	
	48.344	1.85262	
	46.5562	22.8938	1 cme and/or 1,3 ccmcc
	44.9064	10.8003	1,3 cme
	42.0842	16.824	
٠	40.7845	117.364	2 eme
	40.5777	113.702	1,3 eme
	40.3336	136.742	1,3 eme
	39.5591	15.0962	methylene from 2 cmc
			or/and 2 cme
	38.7634	18.636	
	38.4716	12.3847	
	38.2488	17.3939	•
	37.2144	17.5837	
	36.721	111.057	
	36.2913	11.0136	•
	35.8776	22.0367	
	35.6176	90.3685	
	34.5248	15.734	
	34.1959	24.7661	
	33.0182	14.0261	
	31.8671	238.301	
	31.4056	20.6401	•
	30.8433	11.2412	
	30.4613	20.2901	
	30.0104	62.2997	
	29.7133	78.3272	
	29.2359	31.6111	
	28.9653	53.5526	
	28.6577	64.0528	
	26.9813	17.6335	
	26.3925	4.51208	
	25.9363	5.6969	
	24.2971	1.70709	
	22.9019	9.13305	2B ₄
	22.6048	14.3641	2B ₅ +, 2EOC
	19.7349	10.124	1B ₁
	19.1991	2.00384	^{1B} 1
	17.5811	2.28331	end group
	13.8783	26.3448	1B ₄ +, 1EOC
	12.6264	19.6468	end group
	10.9501	4.96188	1B ₂

Example 182

1-Pentene (10 ml) and cyclopentene (10 ml) were copolymerized in 20 ml of o-dichlorobenzene solvent according to example 180. After 72 h, the unreacted monomers and part of the solvent were removed in vacuo to give 3.75 g highly viscous fluid. Analysis by 1H NMR showed that this material contained 1.81 g of copolymer; the remainder was o-dichlorobenzene. NMR spectrum was very similar to poly(ethylene-co-10 cyclopentene) in Example 181. Integration shows 35 mole % cyclopentene in this copolymer. Analysis of the poly(1-pentene) part of the spectrum (omitting peaks due to cyclopentyl units) shows 62 methyl carbons per 1000 methylene carbons. The fraction of ω ,1-15 enchainment (chain straightening) in this section is Based on quantitative 13C analysis, the distribution of branches per 1000 methylene carbons is Methyl (36), Propyl (7), and ≥Amyl (20). DSC (first heat: -150 to 150 °C, 15 °C/min; first cool: 150 to -20 150 °C, 15 °C/min; second heat: -150 to 150 °C, 15 ° C/min,; values of second heat reported): Tg = -19 °C, Tm = 50 °C (24 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as linear polyethylene using universal calibration theory):

25 Mn=14,900 Mw=27,300 Mw/Mn=1.82

Example 183

A 100 mL autoclave was charged with chloroform (40 mL), methyl acrylate (10 mL), {[(2,6-EtPh)_2DABMe_2]PdMe(NCMe)}BAF (0.100 g, 0.073 mmol), and ethylene (2.1 MPa). The reaction mixture was stirred under 1.4 MPa of ethylene for 180 min; during this time the temperature inside the reactor remained between 25 and 26°C. The ethylene pressure was then vented, and the crude reaction mixture discharged from the reactor. The reactor was washed with 2 x 50 mL of chloroform. The washings were added to the crude reaction mixture; 250 mL of methanol was added to the resulting solution. After standing overnight, the polymer product had

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recipitated from solution; it was isolated by decanting off the chloroform/methanol solution, and dried giving 3.91 g of an extremely viscous oil. NMR of this material showed it to be ethylene/methyl acrylate copolymer, containing 1.1 mole% methyl acrylate. The polymer contained 128 methyl-ended hydrocarbon branches per 1000 methylenes, and 7 methyl ester ended branches per 1000 methylenes.

Example 184

A solution of $\{[(Np)_2DABMe_2]PdMe(NCMe)\}SbF_6^-(0.027)$ g, 0.02 mmol) in 5 mL CDCl₃ was agitated under 1.4 MPa of ethylene for 3 h; during this time the temperature inside the reactor varied between 25 and 40°C. of the solution indicated the presence of ethylene oligomers. Mn was calculated on the basis of 1H NMR integration of aliphatic vs. olefinic resonances to be The degree of polymerization, DP, was calculated on the basis of the ¹H NMR spectrum to be 3.8; for a linear polymer this would result in 500 methyl-ended branches per 1000 methylenes. However, based on the ¹H 20 NMR spectrum the number of methyl-ended branches per 1000 methylenes was calculated to be 787.

Example 185

[(2-t-BuPh)2DABMe2]NiBr2

A Schlenk tube was charged with 0.288 g (0.826 25 mmol) of (2-t-BuPh)2DABMe2, which was then dissolved in 15 mL of CH2Cl2. This solution was cannulated onto a suspension of (DME)NiBr2 (0.251 g, 0.813 mmol) in 15 mL of CH2Cl2. The reaction mixture was allowed to stir overnight, resulting in a deep red solution. 30 solution was filtered and the solvent evaporated under The remaining orange, oily residue was washed with ether (2 \times 10 mL) and dried under vacuum to give an orange/rust powder (0.36 g, 78%).

Example 186

[(2-t-BuPh)2DABAn]NiBr2

(2-t-BuPh) 2DABAn (0.202 g, 0.454 mmol) and (DME)NiBr2 (0.135 g, 0.437 mmol) were combined and

tirred in 25 mL of CH₂Cl₂, as in Example 185. An orange/rust solid was isolated (0.18q, 62%).

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Example 187

[(2,5-t-BuPh)₂DABAn]NiBr₂

The corresponding diimine (0.559 g, 1.00 mmol) and (DME)NiBr₂ (0.310 g, 1.00 mmol) were combined and stirred in 35 mL of CH₂Cl₂, as was done in Example 185. An orange solid was isolated (0.64 g, 83%).

Examples 188-190

10 Polymerizations were carried out at 0°C and under 1 atmosphere of ethylene pressure. The (diimine) NiBr2 complex $(1.4-1.7 \times 10^{-5} \text{ mol})$ was placed into a flamedried Schlenk flask and dissolved in 100 mL of toluene. The flask was placed under ethylene and cooled in an 15 ice bath. Polymerization was initiated by addition of 100 equivalents (1.5 mL 10% soln in toluene) of methylaluminoxane (MAO). The reaction mixture was stirred for 30 or 120 minutes at constant temperature followed by quenching with 6M HCl. Polymer was 20 precipitated from the resulting viscous solution with acetone, collected via filtration, and dried under vacuum for 24 h. A summary of results is shown below.

	Ex No.	Catalyst
	188	[(2-t-BuPh) ₂ DABMe ₂]NiBr ₂
25	189	[(2-t-BuPh) ₂ DABAn]NiBr ₂
	190	[(2,5-t-BuPh)2DABAn]NiBr2

Exam.	Catalyst (10 ⁻⁵ mol)	Conditions	Yield (g)	TO/hr mol
188	(1.7)	0°C. 120 m	9.88	10,500
189	(1.4)	0°C. 30 m	8.13	40,500
190	(1.5)	0°C. 30 m	6.60	31,000

Examples 191-196

General Procedure. The procedure of Example 84 for the homopolymerization of ethylene) was followed with the exception that the acrylate was added to the

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eaction mixture at -78°C immediately following the addition of 50 mL of CH₂Cl₂. Polymerizations are at room temperature (rt) and 1 atm ethylene unless stated otherwise. The copolymers were generally purified by filtering an Et₂O or petroleum ether solution of the polymer through Celite and/or neutral alumina. ¹H and ¹³C NMR spectroscopic data and GPC analysis are consistent with the formation of random copolymers. In addition to the polyethylene resonances, the following resonances diagnostic of acrylate incorporation were observed:

Methyl Acrylate: ¹H NMR (CDCl₃, 400 MHz) δ 3.64 (s, OMe), 2.28 (t, J = 7.48, OCH₂), 1.58 (m, OCH₂CH₂); ¹³C NMR (C₆D₆, 100 MHz) δ 176 (C(O)), 50.9 (C(O)OMe).

Fluorinated Octyl Acrylate (FOA. 3M Co. Minneapolis, MN): 1 H NMR (CDCl₃, 400 MHz) δ 4.58 (t, J = 13.51, OCH₂(CF₂)₆CF₃), 2.40 (t, J = 7.32, C(O)CH₂), 1.64 (m, C(O)CH₂CH₂); 13 C NMR (CDCl₃, 100 MHz) δ 172.1 (C(O)), 59.3 (t, J_{CF} = 27.0, OCH₂(CF₂)₆CF₃).

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Ex.	Catalyst (R), conc. (10 ⁻³ Molar)	Acrylate, conc. (Molar)	Rxn Time (h)	Yield (g)	t Acry- late Inc. molt/wtt	# CH3/ 1000 CH ₂	Mw	Mn	PDI
191	Me, 2.3	0 Me, 6.7	24 ^a	≈0.5	10.9/ 27.3	134			
192	Me, 1.4	0 Me, 1.1	48	3.94	2.7/ 7.84	114	77000	56400	1.4 b
193	Me, 2.0	FOA, .74	24	27.5	0.80/	110			
194	Me, 2.0	FOA, 1.3	24	20.7	0.80/	126			
195	H, 2.0	FOA, .74	24	1.49	0.31/	144			
196	2.00	FOA; .74	24	2.00	0.71/	135			

^aFinal 3 h at 50°C.

bTHF, PMMA standards.

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cCatalyst is { [(2,6-i-

PrPh) DABAn) PdCH₂CH₂CH₂C(0) OCH₂ (CF₂) ₆CF₃) }BAF

Examples 197-203

In Examples 197-203, structures of the type 5 represented by (VI) and (IX) are described.

Example 197

 $\{[(2.6-i-PrPh)_2DABMe_2]PdMe(H_2C=CH_2)\}BAF^-$ and $\{[(2.6-i-PrPh)_2DABMe_2]Pd(P)H_2C=CH_2)\}BAF^-$

In a drybox under an argon atmosphere, an NMR tube was charged with ~0.01 mmol of ({[(2,6-i-PrPh)₂DABMe₂]PdMe}₂(μ-Cl))BAF /[(Na(OEt₂)₂BAF or NaBAF] or {[(2,6-i-PrPh)₂DABMe₂]PdMe(OEt₂)}BAF. The tube was then capped with a septum, removed from the drybox, and cooled to -78°C. Via gastight syringe, 700 μL of CD₂Cl₂ was then added to the NMR tube and the septum was wrapped with Parafilm. The tube was shaken very briefly in order to dissolve the palladium complex. After acquiring a spectrum at -80°C, 1 - 10 equiv of olefin was added to the -78°C solution via gastight

- syringe, ant the olefin was dissolved in the solution by briefly shaking the NMR tube. The tube was then transferred to the cold NMR probe and spectra were acquired. This olefin complex was prepared from both precursors using one equiv of ethylene: 1H NMR
- 25 (CD₂Cl₂, 400 MHz, -60°C) δ 7.72 (s, 8, BAF: C₀), 7.54 (s, 4, BAF: C_p), 7.4 7.0 (m, 6, H_{aryl}), 4.40 (s, 4, H₂C=CH₂), 3.38 (br m, 4, O(CH₂CH₃)₂), 2.69 (septet, 2, J = 6.73, CHMe₂), 2.63 (septet, 2, J = 6.80, C'HMe₂), 2.34 and 2.23 (s, 3 each, N=C(Me)-C'(Me)=N), 1.33 (d,
- 30 6, J = 6.80, C'HMeMe'), 1.25 (d, 6, J = 6.50, CHMeMe'), 1.14 (d, 6, J = 7.00, CHMeMe'), 1.10 (br m, 6, $O(CH_2CH_3)_2$), 1.07 (d, 6, J = 6.80, C'HMeMe'), 0.18 (PdMe); ¹³C NMR (CD₂Cl₂, 100 MHz, -60°C) δ 180.3 and 174.7 (N=C-C'=N), 161.5 (q, $J_{BC} = 49.6$, BAF: C_{ipso}),
- 35 143.3 and 141.7 (Ar, Ar': C_{ipso}), 134.4 (BAF: C_o), 128.6 (Ar: C_p), 128.4 (q, J_{BC} = 32.3, BAF: C_m), 127.7 (Ar': C_p), 124.7 and 124.4 (Ar, Ar': C_o), 117.3 (BAF: C_p), 91.7 (J_{CH} = 160.7, $H_2C=CH_2$), 65.8 (O(CH_2CH_3)₂), 28.9

CHMe₂), 28.8 (C'HMe₂), 24.1, 23.4, 22.9 and 22.7 (CHMeMe', C'HMeMe'), 21.7 and 21.5 (N=C(Me)=C'(Me)=N), 15.0 (OCH₂CH₃)₂), 4.3 (PdMe).

In the presence of 5 equiv of ethylene, chain growth was observed at -35°C. Spectral data for {[(2,6-i-PrPh)2DABMe2]Pd(P)(CH2=CH2)}BAF [wherein P is as defined for (VI)] intermediates (CD2Cl2, 400 MHz, -35°C) are reported in the following table:

	{[(2,6	-i-PrPh) ₂ [OABMe ₂]I	Pd[(CH ₂) _r	CH3](H2	C=CH2)}	+BAF-			
	H2C=CH2		N=C(Me)-C'(Me)=N					Pd(CH ₂) _n Me		
n	mult.	, δ	mult.	δ	mult.	δ	mult	J	δ	
0	s	4.42	s	2.35	s	2.24	s		0.22	
2	s	4.36	. s	2.37	s	2.22	t	7.00	0.39	
4	S	4.36	s s	2.37	s	2.22	t	7.20	0.62	

10

Addition of 15 more equiv of ethylene and warming to room temperature leads to complete consumption of ethylene and the observance of a single organometallic species: ^1H NMR (CD₂Cl₂, 400 MHz, 24.0°C) δ 7.74 (s, 8, BAF: C_o), 7.19 (s, 4, BAF: H_p), 2.85 (br m, 4, CHMe₂, C'HMe₂), 2.36 and 2.23 (s, 3 each, N=C(Me) - C'(Me)=N), 1.5 - 1.0 (CHMeMe', C'HMeMe'), 1.29 (Pd(CH₂)_nCH₃), 0.89 (Pd(CH₂)_nCH₃).

Example 198

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This olefin complex, $\{[(2,6-i-PrPh)_2DABH_2]PdMe(H_2C=CH_2)\}BAF$, was prepared following the procedure of example 197 by both of the analogous synthetic routes used in example 197, using one equiv of ethylene: 1H NMR $(CD_2Cl_2, 400 \text{ MHz}, -60^{\circ}C)$ δ 8.42 and 8.26 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_o), 7.54 (s, 4, BAF: H_p), 7.42 - 7.29 (m, 6, H_{aryl}), 4.60 (s, H₂C=CH₂), 3.37 (q, 4, J = 7.03, $(O(CH_2CH_3)_2)$, 2.89 (septet, 2, J = 6.71, CHMe₂), 2.76 (septet, 2, J = 6.68, C'HMe₂), 1.35 (d, 6, J = 6.72, C'HMeMe'), 1.29

d, 6, J = 6.79, CHMeMe'), 1.15 (d, 6, J = 6.72, CHMeMe'), 1.09 (d, 6, J = 6.54, C'HMeMe'), 1.15 (t, 6, J = 7.34, $O(CH_2CH_3)_2$), 0.46 (s, 3, PdMe); ¹³C NMR (CD_2Cl_2 , 400 MHz, -60°C) δ 167.7 (J_{CH} = 182, N=C(H)), 162.8 (J_{CH} = 182, N=C'(H)), 161.4 (q, J = 49.8, BAF: C_{ipso}), 140.2 and 139.8 (Ar, Ar': C_{ipso}), 138.6 and 137.3 (Ar, Ar': C_o), 134.4 (BAF: C_o), 129.2

 C_m), 124.3 and 124.0 (Ar, Ar': C_m), 124.2 (q, J_{CF} = 272.5; BAF: CF_3), 117.3 (BAF: C_p), 92.7 (J_{CH} = 162.5, $H_2C=CH_2$), 65.8 (O(CH_2CH_3)₂), 28.9 and 28.7 ($CHMe_2$ and $C'HMe_2$), 25.1, 24.0, 22.0 and 21.9 (CHMeMe', C'HMeMe'), 15.12 (J_{CH} = 139.2, PdMe), 15.09 (O(CH_2CH_3)₂).

and 129.1 (Ar, Ar': C_p), 128.3 (q, $J_{CF} = 32.2$, BAF:

In the presence of 10 equiv of ethylene, chain growth was monitored at -35°C . Diagnostic ¹H NMR spectral data (CD₂Cl₂, 400 MHz, -35°C) for the second title compound are reported in the following table:

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$\{[(2.6-i-PrPh)_2DABH_2]Pd[(CH_2)_nCH_3](H_2C=CH_2)\}^+BAF^-$									
		<i>H</i> ₂ C=	=C <i>H</i> 2	Pd(CH ₂) _n Me					
n	mult.	δ	mult.	δ	mult.	δ	mult	J	δ
0 <i>a</i>	s	8.42	s	8.27	br s	4.6	s		0.50
2^b	s	8.41	s	8.24	br s	4.6	t	7.85	0.36
4	s	8.41	s	8.24	br s	4.6	t	7.15	0.62
6	s	8.41	S	8.24	br s	4.6	t	7.25	0.76
>6	s	8.41	s	8.24	br s ^c	4.6	m		0.85d

^aFor n = 0: δ 2.91 and 2.71 (septet, 2 each,

20 CHMe₂, C'HMe₂), 1.38, 1.32, 1.18 and 1.12 (d, 6 each, CHMeMe', C'HMeMe'). b For n > 0: δ 2.91 and 2.71 (septet, 2 each, CHMe₂, C'HMe₂), 1.37, 1.35, 1.16 and 1.11 (d, 6 each, CHMeMe', C'HMeMe'). In the absence of free ethylene, bound ethylene appears as a sharp singlet at 4.56 ppm. $^{d}\delta$ 1.27 (Pd(CH₂)_nCH₃).

After the ethylene was consumed at -35° C, the sample was cooled to -95° C. Broad upfield multiplets were observed at -7.2 to -7.5 ppm and -3.0 to -8.5 ppm. The sample was then warmed to room temperature

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and a spectrum was acquired. No olefins were detected, the upfield multiplets were no longer observable, and a single organometallic species was present: 1 H NMR (CD₂Cl₂, 400 MHz, 19.8°C) δ 8.41 and 8.28 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_O), 7.56 (s, 4, BAF: H_D), 3.09 (m, 4, CHMe₂, C'HMe₂), 1.35, 1.32, 1.26 and 1.22 (d, 6 each, J = 6.5-6.8, CHMeMe', C'HMeMe'), 1.27 (Pd(CH₂)_nCH₃), 0.88 (Pd(CH₂)_nCH₃).

A second spectrum was acquired 12 minutes

10 later at room temperature. Substantial decomposition
of the organometallic species was observed.

Example 199

 $\{ [(2,6-i-PrPh)_2DABH_2] PdMe (H_2C=CH_2) \} BAF^-$ This olefin complex, $\{ [(2,6-$

- 20 4, BAF: H_p), 7.4 6.4 (m, 6, H_{aryl}), 4.56 (s, 4, H₂C=CH₂), 2.19 and 2.16 (s, 6 each, Ar, Ar': Me), 0.31 (s, 3, PdMe).

In the presence of 10 equiv of ethylene (eq. 3), olefin insertion was monitored at -30°C and the production of cis- and trans-2-butenes was observed.

This olefin complex, {[(2,6-i-

Example 200

 $\{[(2,6-i-PrPh)_2DABMe_2]PdMe(H_2C=CHMe)\}BAF^-$

PrPh) 2DABMe2 PdMe (H2C=CHMe) BAF, was prepared following the procedure of Example 197, using { [(2,6-i-PrPh)2DABMe2] PdMe (OEt2) BAF and one equiv of propylene: 1H NMR (CD2Cl2, 400 MHz, -61°C) δ 7.73 (s, 8, BAF: H0), 7.55 (s, 4, BAF: Hp), 7.4 - 7.0 (m, 6, Haryl), 5.00 (m, 1 H2C=CHMe), 4.24 (d, 1, J = 9.1, HH'C=CHMe), 4.23 (d,

35 1, J = 14.8, HH'C=CHMe), 3.38 (br q, 4, J = 6.50,
O(CH₂CH₃)₂), 2.84 (septet, 1, J = 6.5, Ar: CHMe₂), 2.68
(m, 3, Ar: C'HMe₂; Ar': CHMe₂, C'HMe₂), 2.32 and 2.22
(s, 3 each, N=C(Me)-C'(Me)=N), 1.63 (d, 3, J = 6.40,

```
I_2C=CHMe), 1.35, 1.30, 1.25, 1.1, 1.1, 1.04 (d, 3 each,
    J = 6.4 - 6.7, Ar: C'HMeMe'; Ar': CHMeMe', C'HMeMe'),
    1.24 and 1.1 (d, 3 each, J = 6.4, Ar: CHMeMe'), 1.1 (m,
    6, O(CH_2CH_3)_2, 0.28 (PdMe); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz,
    -61^{\circ}C) \delta 179.9 and 174.7 (N=C-C'=N), 161.5 (q, J<sub>BC</sub> =
    49.7, BAF: Cipso), 138.8, 137.9, 137.8, 137.7, 137.0
    and 136.9 (Ar: Cipso, Co, Co'; Ar': Cipso, Co, Co');
    134.4 (BAF: C_0), 128.6 and 128.5 (Ar: C_p, C_p), 128.4
    (q, J_{CF} = 31.6, BAF: C_m), 124.8, 124.7, 124.4 and 124.4
10
    (Ar: C_m, C_m'; Ar': C_m, C_m'), 124.2 (q, J_{CF} = 272.5,
    BAF: CF_3), 117.3 (BAF: C_p), 116.1 (J_{CH} = 155.8,
    H_2C=CHMe), 85.6 (J<sub>CH</sub> = 161.4, H_2C=CHMe), 65.8
     (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 28.9, 28.7, 28.7, 28.7 (Ar: CHMe<sub>2</sub>,
    C'HMe2; Ar': CHMe2, C'HMe2), 24.5, 23.9, 23.5, 23.4,
    22.9, 22.9, 22.8, 22.2, 21.71, 21.65, 20.9 (H<sub>2</sub>C=CHMe;
    Ar: CHMeMe', C'HMeMe'; Ar': CHMeMe', C'HMeMe', N=C(Me)-
    C'(Me) = N), 16.9 (J<sub>CH</sub> = 137.5, PdMe), 15.0 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).
                                 Example 201
              \{[(2,6-i-PrPh)_2DABH_2]PdMe(H_2C=CHMe)\}BAF^- and
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                \{[(2,6-i-PrPh)_2DABH_2]Pd(P)(H_2C=CHMe)\}BAF^-
          This olefin complex, {[(2,6-i-
    PrPh), DABH, PdMe (H, C=CHMe) BAF, was prepared following
    using both of the synthetic routes used in Example 197,
    using one equiv of propylene: 1H NMR (CD2Cl2, 400 MHz,
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    -80 °C) \delta 8.40 and 8.24 (s, 1 each, N=C(H)-C'(H)=N),
    7.72 (s, 8, BAF: H_0), 7.53 (s, 4, BAF: H_p), 7.40 -7.27
    (m, 6, H_{aryl}), 5.41 (br m, H_2C=CHMe), 4.39 (d, 1, J =
    8.09, HH'C=CHMe), 4.14 (br d, 1, J = 15.29, HH'C=CHMe),
    3.10 (br m, 1, CHMe<sub>2</sub>), 2.87 (overlapping septets, 2,
    C'HMe2, C''HMe2), 2.59 (br septet, 1, C'''HMe2), 1.64
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    (d, J = 6.07, H_2C=CHMe), 1.39 and 1.03 (d, 3 each, J =
    6.4, CHMeMe'), 1.27, 1.27, 1.14 and 1.1 (d, 3 each, J =
    5.9 - 6.7, C'HMeMe', C''HMeMe'), 1.23 and 1.1 (d, 3
    each, J = 6.8, C'''HMeMe'), 0.47 (PdMe); ^{13}C NMR
    (CD_2Cl_2, 100 \text{ MHz}, -80^{\circ}C) \delta 167.1 (JCH = 181.6, N=C(H)),
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    163.0 (JCH = 182.1, N=C'(H)), 161.3 (q, JBC = 50.0,
    BAF: Cipso), 140.5 and 140.0 (Ar, Ar': Cipso), 138.5,
    138.3, 137.7 and 137.2 (Ar: C_0, C_0'; Ar': C_0, C_0'),
```

.34.2 (BAF: C_O), 128.9 and 128.8 (Ar, Ar': C_p), 128.1
 (q, J_{CF} = 31.1, BAF: C_m), 124.0 (q, J_{CF} = 272.5, BAF:
 CF₃), 124.6, 123.8, 123.8 and 123.6 (Ar: C_m, C_m'; Ar':
 C_m, C_m'), 117.1 (BAF: C_p), 116.4 (J_{CH} = 160.3,
 H₂C=CHMe), 85.4 (J_{CH} = 159.9, H₂C=CHMe), 65.7
 (O(CH₂CH₃)₂), 29.2, 28.7, 28.5 and 28.0 (Ar: CHMe₂,
 C'HMe₂; Ar': CHMe₂, C'HMe₂), 26.0, 24.4, 24.03, 23.97,
 23.7, 21.9, 21.8, 21.7 and 21.6 (H₂C=CHMe; Ar: CHMeMe',
 C'HMeMe'; Ar': CHMeMe', C'HMeMe'), 16.6 (J_{CH} = 142.1,
 PdMe), 15.0 (O(CH₂CH₃)₂).

In the presence of 10 equiv of propylene, chain growth was monitored at -20° C, thus enabling {[(2,6-i-PrPh)₂DABH₂]Pd[(CHMeCH₂)Me](H₂C=CHMe)}BAF, intermediates to be observed (CD₂Cl₂, 400 MHz, -20°C):

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3, PdMe).

	$\{[(2.6-i-PrPh)_2DABMe_2]Pd((CHMeCH_2)_nMe)(H_2C=CHMe)\}^+BAF^-$												
N=CHC'H=N		<i>H</i> H	HH'C=CHMe HH'C=CHMe		C=C <i>H</i> Me		(CHMeCH ₂) _n Me						
n ´	δ	δ	mult	J	δ	mult	J	δ	mult	δ	mult	J	δ
0	8.40	8.26	đ	14.4	4.25	d	8.6	4.47	m	5.45	s		0.59
1	8.38	8.24	d	14.4	3.98	d	7.4	4.25	m	5.55	t l	7.1	0.51
>1	8.39	8.23	d	13.7	4.07	d	8.0	4.41	m	5.42			

Example 202

The compound {[(2,6-i-

Isomerization to *cis-* and *trans-2-*butene began at -78°C and was monitored at -15°C along with chain

prowth. For Pd[P] species, formation of the 1-butene complex occurred selectively in the presence of cisand trans-2-butene. Consumption of all olefins was observed at 20°C.

Examples 203

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 $\{[(2,6-i-PrPh)_2DABH_2]PdMe(CH_3CH=CHCH_3)\}BAF^{-1}$

Experiments involving the reaction of the bispalladium $(\mu\text{-Cl})$ compound/NaBAF (as in Example 197) with trans-2-butene and the bispalladium $(\mu\text{-Cl})$ compound alone with cis-2-butene led to partial formation of the corresponding olefin complexes. An equilibrium was observed between the ether adduct and the olefin adduct when a compound of the type $\{[(2,6-i-$

PrPh)₂DABH₂] PdMe (OEt₂) }BAF was reacted with one equiv of cis- or trans-2-butene. Addition of excess 2-butene led to complete formation of the olefin adduct. Chain growth, which was monitored at 0°C to room temperature, led to complete consumption of butenes. Some butene isomerization occurred during the course of the

oligomerization and small amounts of β-hydride elimination products (disubstituted internal olefins and trisubstituted olefins) were observed. Oligomer methylene and methyl groups were observed at 1.3 and 0.8 ppm, respectively. Diagnostic ¹H NMR spectral data for the butene complexes follows:

 $\left\{ \left[(2,6\text{-i-PrPh})_{2} DABH_{2} \right] PdMe \left(trans-CH_{3} CH=CHCH_{3} \right) \right\} BAF^{-}. \\ ^{1}H \ NMR \ \left(CD_{2} Cl_{2},\ 400\ MHz,\ -39^{\circ}C \right) \ \delta \ 8.43 \ and \ 8.29 \ (s,\ 1) \\ each,\ N=C(H)-C(H)=N) \ , \ 5.27 \ and \ 4.72 \ (m,\ 1) each, \\ CH_{3} CH=C^{\circ}HCH_{3} \),\ 0.73 \ \left(PdMe \right) \ ; \ ^{1}C \ NMR \ \left(CD_{2} Cl_{2},\ 100\ MHz,\ -95^{\circ}C \right) \ \delta \ 166.8 \ \left(J_{CH} = 181.5,\ N=C(H) \right) \ , \ 163.2 \ \left(J_{CH} = 179.8,\ N=C^{\circ}(H) \right) \ , \ 161.2 \ \left(g,\ J_{BC} = 49.5,\ BAF:\ C_{ipso} \right) \ , \ 141.3 \ and \\ 139.9 \ \left(Ar,\ Ar':\ C_{ipso} \right) \ , \ 138.4 \ , \ 138.2 \ , \ 138.0 \ and \ 137.0 \\ \left(Ar,\ Ar':\ C_{o},\ C_{o}' \right) \ , \ 134.0 \ \left(BAF:\ C_{o} \right) \ , \ 128.74 \ and \ 128.71 \\ \left(Ar,\ Ar':\ C_{p} \right) \ , \ 128.0 \ \left(g,\ J_{CF} = 31.9,\ BAF:\ C_{m} \right) \ , \ 125.4 \\ \left(J_{CH} = 150.0,\ free\ MeCH=CHMe) \ , \ 123.8 \ \left(g,\ J_{CF} = 272.5,\ BAF:\ CF_{3} \right) \ , \ 124.8 \ , \ 123.7 \ , \ 123.5 \ and \ 123.4 \ \left(Ar,\ Ar':\ C_{o},\ C_{o}' \right) \ , \ 117.0 \ \left(BAF:\ C_{p} \right) \ , \ 107.0 \ and \ 106.8 \ \left(J_{CH}-152,\ MeCH=C'HMe) \ , \ 65.6 \ \left(free\ O(CH_{2}CH_{3})_{2} \right) \ , \ 29.5 \ , \ 28.3 \ , \ 27.6 \ , \ \right.$

26.5, 24.1, 23.8, 23.6, 21.5, 21.3, 21.2, **2074 19.9** 19.6, 17.9, 17.5 (Ar, Ar': CHMeMe', C'HMeMe'; MeCH=C'HMe), 17.7 (free MeCH=CHMe), 15.0 (PdMe), 14.7 (O(CH₂CH₃)₂).

References for the synthesis of bis(oxazoline)

ligands and their transition metal complexes: Corey,
E. J.; Imai, N.; Zang, H. Y. J. Am. Chem. Soc. 1991,

113, 728-729. Pfaltz, A. Acc. Chem. Res. 1993, 26,

339-345, and references within.

Example 204

2,2-bis{2-[4(S)-methyl-1,3-oxazolinyl]}propane
(500 mg, 2.38 mmol) was dissolved in 10 mL CH₂Cl₂ in a
Schlenk tube under a N₂ atmosphere. This solution was
added via cannula to a suspension of (1,2dimethoxyethane)NiBr₂ (647 mg, 2.10 mmol) in 30 mL of
CH₂Cl₂. The solution was stirred for 18 hours. The
solvent was evaporated under reduced pressure. The
product, 2,2-bis{2-[4(S)-methyl-1,3oxazolinyl]}propaneNi(Br₂), was washed with 3 x 15 mL
of hexane. The product was isolated as a purple powder
(0.85 g, 84% yield).

Example 205

The product of Example 204 (14.2 mg, 3.3×10^{-5} mol) and toluene (75 mL) were combined in a Schlenk flask under 1 atmosphere ethylene pressure. The solution was cooled to 0°C, and 3.0 mL of a 10% MAO (100 eq) solution in toluene was added. The resulting yellow solution was stirred for 40 hours. The oligomerization was quenched by the addition of $\rm H_2O$ and a small amount of 6 M HCl. The organic fraction was separated from the aqueous fraction, and the toluene was removed under reduced pressure. A colorless oil resulted (0.95 g of oligomer). This illustrates that polymerization may be effected by such Pd, Ni and/or Co

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positions of the oxazoline ring by hydrocarbyl and substituted hydrocarbyl groups.

Example 206

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[(COD)PdMe(NCMe)]+BAF-

To CODPdMeCl (100mg, 0.37 mmol) was added a solution of acetonitrile (0.08 mL, 1.6 mmol) in 25 mL CH₂Cl₂. To this colorless solution was added Na⁺BAF⁻ (370 mg, 0.4 mmol). A white solid immediately precipitated. The mixture was stirred at -20°C for 2 hours. The solution was concentrated and filtered. Removal of solvent under reduced pressure resulted in a glassy solid. 1 H NMR (CD₂Cl₂) δ 5.78 (mult, 2H), δ 5.42 (mult, 2H), δ 2.65 (mult, 4H), δ 2.51 (9mult, 4H), δ 2.37 (s, 3H, NCMe), δ 1.19 (s, 3H, Pd-Me), δ 7.72 (s, 8, BAF⁻, H_O), δ 7.56 (s, 4, BAF⁻, H_D).

Example 207

[2,6-(i-Pr)₂PhDABH₂]NiBr₂ (10 mg, 1.7 x 10⁻⁵ mol), toluene (13 mL), and 1-hexene (38 mL) were combined in a Schlenk flask under an argon atmosphere. A 10% MAO solution (1.5 mL, 100 eq) in toluene was added to a suspension of the diimine nickel dihalide. The resulting purple solution was stirred at room temperature for 1 hour. The polymerization was quenched and the polymer precipitated from acetone. The resulting colorless polymer was dried in vacuo (2.5 g). GPC (toluene, polystyrene standards) $M_{\rm n}$ = 330,000; $M_{\rm m}$ = 590,000; $M_{\rm n}/M_{\rm w}$ = 1.8.

Example 208

[(2,6-i-PrPh)₂DABH₂]NiBr₂ (10 mg, 1.7 x 10⁻⁵ mol) was added to a solution which contained toluene (30 mL) and 1-octene (20 mL). A 10% solution of MAO (1.5 mL, 100 eq) in toluene was added. The resulting purple solution was allowed to stir for 4 hours at room temperature. Solution viscosity increased over the duration of the polymerization. The polymer was precipitated from acetone and dried *in vacuo* resulting

.n 5.3 g of copolymer. $M_n = 15,200$; $M_w = 29,100$; $M_w/M_n = 1.92$.

Example 209

 $[(2,6-i-PrPh)_2DABMe_2]Ni(CH_3)_2$ (20 mg, 4.1 x 10⁻⁵ 5 mol) and MAO (35.7 mg, 15eq) were combined as solids in an NMR tube. The solid mixture was cooled to -78°C and dissolved in 700 μ L of CD₂Cl₂. While cold, 10 μ L of ether d10 was added to stabilize the incipient cation. ¹H NMR spectrum were recorded at 253, 273, and 293°K. 10 It was apparent that the starting nickel dimethyl complex was disappearing and a new nickel complex(es) was being formed. Activation of the dimethyl complex was occurring through methane loss (s, δ 0.22). After 2 hours at 293°K all of the starting species had 15 disappeared. To test for ethylene polymerization activity, 5000 µL (10eq) of ethylene was added via gas tight syringe to the solution at -78°C. consumption of ethylene was monitored by ¹H NMR spectroscopy. The onset of ethylene uptake was 20 observed at 223°K and all of the ethylene was consumed upon warming the probe to 293°K. The persistence of the Ni-Me signal during the experiment suggests that under these conditions propagation is faster than initiation. Solid polyethylene was observed upon 25 removing the NMR tube from the probe.

Example 210

[(2,6-i-PrPh)₂DABAn]NiBr₂ (12 mg, 1.7 x 10⁻⁵ mol) was combined with toluene (50 mL) and 1-hexene (25 mL) under a N₂ atmosphere. Et₂AlCl (0.01 mL, 10 eq) was added to the polymerization mixture. The resulting purple solution was allowed to stir for 4 hours. After 4 hours the polymerization was quenched and the polymer precipitated from acetone. The polymerization yielded 2.05 g poly(1-hexene) (731 TO). (GPC, toluene, polystyrene standards) M_n = 305,000; M_w = 629,000; M_w/M_n = 2.05. T_g = -57°C, T_m = 52°C. T_m = -57°C, T_g = -20°C. ¹H NMR (C₆D₅Cl, 142°C) 10 methyls per 100

rarbons. This number is significantly less than would be expected for strictly atactic 1-hexene.

Example 211

Concentration dependence on catalyst activity in nickel catalyzed polymerization of α -olefins. A series 5 of homopolymerizations of 1-hexene were run at 10%, 15%, 20%, 30%, 40%, and 75% 1-hexene by volume. each of the above cases 10 mg of [(2,6-i-PrPh) 2DABH2] NiBr2 was taken up in toluene and 1-hexene 10 (50 mL total volume 1-hexene + toluene). All of the polymerizations were run at 25°C and activated by the addition of 1.5 mL of a 10% MAO solution in toluene. The polymerizations were stirred for 1 hour and quenched upon the addition of acetone. The polymer was 15 precipitated from acetone and dried in vacuo. volume 1-hexene yielded 2.5 g poly(1-hexene), 15% by volume 1-hexene yielded 2.6 g poly(1-hexene), 20% by volume 1-hexene yielded 3.0 g poly(1-hexene), 30% by volume 1-hexene yielded 2.6 g poly(1-hexene), 40% by 20 volume 1-hexene yielded 2.6 g poly(1-hexene), 75% by volume 1-hexene yielded 2.5 g poly(1-hexene).

Example 212

 $FeCl_2$ (200 mg, 1.6 mmol) and 20 ml of CH_2Cl_2 were combined in a Schlenk flask under an argon atmosphere. In a separate flask, 550 mg (2,6-i-PrPh)₂DABMe₂ and 20 ml CH₂Cl₂ were combined, resulting in a yellow solution. The ligand solution was slowly (2 hr) transferred via cannula into the suspension of FeCl2. The resulting solution was stirred at 25°C. After 4 hr. the solution was separated from the unreacted FeCl₂ 30 by filter cannula (some purple solid was also left behind). The solvent was removed in vacuo to give a purple solid (0.53 g, 71% yield). A portion of the purple solid was combined with 50 ml of toluene under 1 atm of ethylene. The solution was cooled to 0°C, and 6 35 ml of a 10% MAO solution in toluene was added. The mixture was warmed to 25°C and stirred for 18 hr. polymer was precipitated by acetone, collected by

suction filtration, and washed with 6M HCT, water and acetone. The white polymer was dried under reduced pressure. Yield 13 mg.

Example 213

A 58-mg (0.039-mmol) sample of $\{[(2,6-i-$ 5 PrPh) 2DABMe2] PdCH2CH2CH2C(O)OCH3} BAF was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water. This mixture was pressurized to 5.5 MPa with ethylene and was stirred at 23°C for 68 hr. 10 When the ethylene was vented, the autoclave was found to be full of rubbery polymer: on top was a layer of white, fluffy elastomeric polyethylene, while beneath was gray, dense elastomeric polyethylene. The water was poured out of the autoclave; it was a hazy light 15 blue, containing a tiny amount of emulsified polyethylene; evaporation of the whole aqueous sample yielded a few mg of material. The product was dried under high vacuum to yield 85.5g of amorphous elastomeric polyethylene, which exhibited a glass 20 transition temperature of -61°C and a melting endotherm of -31°C (16J/g) by differential scanning calorimetry. H-1 NMR analysis (CDCl₃): 105 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, 25 results calculated as polyethylene using universal calibration theory): $M_n=42,500$; $M_w=529,000$; $M_w/M_n=12.4$. This example demonstrates the use of pure water as a polymerization medium .

Example 214

A 73-mg (0.049 mmol) sample of {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}BAF was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 3.1 mL (3.3g) of Triton³ X-100 nonionic surfactant. This mixture was pressurized to 5.8 MPa with ethylene and was stirred at 23°C for 17 hr. When the ethylene was vented, most of the emulsion came out the valve due to foaming; it was caught in a flask. There was polymer suspended in the

mulsion; this was filtered to give, after MeOH and acetone washing and air-drying, 2.9g of amorphous polyethylene as a fine, gray rubber powder. filtrate from the suspended polymer was a clear gray solution; this was concentrated on a hot plate to yield recovered Triton[®] X-100 and palladium black. no polymer in the aqueous phase. The elastomeric polyethylene product exhibited a glass transition temperature of -50°C and a melting endotherm of 48°C 10 (5J/g) by differential scanning calorimetry. H-1 NMR analysis (CDCl₃): 90 methyl carbons per 1000 methylene carbons. Gel permeation chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n=31,000$; $M_w=311,000$; $M_w/M_n=10.0$. This example demonstrates the aqueous emulsion polymerization of ethylene in the presence of a nonionic surfactant.

Example 215

20 A 93-mg (0.110-mmol) sample of $\{[(2,6-i-$ PrPh) 2DABMe2] PdCH2CH2CH2C(O)OCH, } +SbF6 was placed in a 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 0.75q (1.4 mmol) of FC-95® anionic fluorosurfactant (potassium perfluorooctansulfonate). This mixture was pressurized to 5.1 MPa with ethylene and was stirred at 23°C for 15 The ethylene was vented; the product consisted of polymer suspended in emulsion as well as some polymer granules on the wall of the autoclave; the emulsion was filtered to give, after MeOH and acetone washing and 30 air-drying, 2.4g of amorphous polyethylene as a fine, gray rubber powder. The hazy blue-gray aqueous filtrate was evaporated to yield 0.76g of residue; hot water washing removed the surfactant to leave 0.43g of dark brown sticky polyethylene rubber. H-1 NMR (CDCl₃) analysis: 98 CH3's per 1000 CH2's. Differential scanning calorimetry: melting point: 117°C (111J/g); glass transition: -31°C (second heat; no apparent Tg on

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emulsion polymerization of ethylene in the presence of a anionic surfactant. This example also demonstrates that a true aqueous emulsion of polyethylene can be obtained by emulsion polymerization of ethylene with these catalysts in the presence of an appropriate surfactant.

Example 216

A 90-mg (0.106-mmol) sample of $\{[(2,6-i-$ PrPh) 2DABMe2] PdCH2CH2CH2C(O)OCH3}+SbF6 was placed in a 10 600-mL stirred autoclave under nitrogen with 150mL of deaerated water; to this was added 0.75g (2.1 mmol) of cetyltrimethylammonium bromide cationic surfactant. This mixture was pressurized to 5.2 MPa with ethylene and was stirred for 66 hr at 23°C. The ethylene was 15 vented; the product consisted of polymer suspended in a dark solution; this was filtered to give, after MeOH and acetone washing and air-drying, 0.13g of amorphous polyethylene as a tacky, gray rubber powder. There was no polymer in the aqueous phase. H-1 NMR (CDCl₃) 20 analysis: 96 CH3's per 1000 CH2's. Differential scanning calorimetry: glass transition: -58°C; melting endotherms: 40° , 86° , 120° C (total: 20J/g). example demonstrates the aqueous emulsion polymerization of ethylene in the presence of a 25 cationic surfactant.

Example 217

An 87-mg (0.103-mmol) sample of $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(0)OCH_3\}^+SbF_6^-$ was placed in a 600-mL stirred autoclave under nitrogen. To this was added 100 mL of dry, deaerated methyl acrylate containing 100 ppm of phenothiazine as a free-radical polymerization inhibitor. The autoclave was stirred and pressurized to 300 psig with ethylene over 5 min. The autoclave was then pressurized to 600 psig with an additional 300 psig of carbon monoxide (300 psig E + 300 psig CO = 600 psig). The reaction was stirred for 20 hr at 23°C as the autoclave pressure dropped to 270

psig. The ethylene was then vented; the autocrave contained a yellow solution which was concentrated by rotary evaporation, taken up in methylene chloride, filtered, and again concentrated to yield 0.18g of dark brown viscous oil. The product was washed with hot acetone to remove the brown catalyst residues and was held under high vacuum to yield 55 mg of a colorless, viscous liquid terpolymer. The infrared spectrum exhibited carbonyl absorbances at 1743 (ester), 1712 (ketone), and 1691 cm⁻¹. H-1 NMR (CDCl₃) analysis: 76CH₃'s per 1000 CH₂; there were peaks at 2.3 (t, CH_2COOR), 2.7 (m, CH_2CO), and 3.66 ppm ($COOCH_3$). polymer contained 3.3 mol% MA (9.4 wt% MA). The carbon monoxide content was not quantified, but the absorbance in the infrared spectrum of the polymer due to ketone was about 1/2 to 2/3 the absorbance due to acrylate This example demonstrates the use of carbon monoxide as a monomer.

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Example 218

20 A 20-mg (0.035-mmol) sample of $NiBr_2[2 NpCH=N(CH_2)_3N=CH-2-Np]$, where Np = naphthyl, (see structure below) was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry deaerated, toluene. Then 0.6 mL of polymethylalumoxane 25 (3.3M) was injected; the light pink suspension became a dark gray-green solution, eventually with black precipitate. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 18 hr, during which time the mixture became a clear yellow 30 solution with black, sticky precipitate. The ethylene was vented; the offgas contained about 3% butenes (90:10 1-butene: trans-2-butene) by gas chromatography (30-m Quadrex GSQ® Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl 35 and methanol and was separated; concentration of the toluene solution followed by acetone rinsing the residue yielded 85 mg of liquid polyethylene. H-1 NMR (CDCl₃) analysis: 209 CH₃'s per 1000 CH₂'s. This

example demonstrates the efficacy of a catalyst with a bis-imine ligand in which the imine groups are not alpha to one another.

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Example 219

A 17-mg (0.027-mmol) sample of [(2,6-i-PrPh) 2DABMe2] ZrCl4 was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the yellow suspension became an orange-yellow solution. The mixture was pressurized with ethylene to 7 psig and was stirred at 23°C for 20 hr, during which time polymer slowly accumulated on the stir bar and eventually rendered the solution unstirrable. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield (after MeOH and acetone washing and air-drying) 1.01g of white, fluffy polyethylene. Differential scanning calorimetry exhibited a melting point of 131°C (124J/g). example demonstrates the efficacy of a Zr(IV) catalyst bearing a diimine ligand.

Example 220

A 14-mg (0.024-mmol) sample of [(2,6-i-PrPh)₂DABMe₂]TiCl₄ was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry; deareated toluene (distilled from Na under N₂). Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the yellow suspension became a dark brown suspension with some precipitate. The mixture was pressurized with ethylene to 7 psig and was stirred at 23°C for 3 hr, during which time polymer accumulated and rendered the solution unstirrable. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield, after MeOH and acetone washing and air-drying, 1.09g of

white, fluffy polyethylene. Differential scanning calorimetry exhibited a melting point of 131°C (161J/g). This example demonstrates the efficacy of a Ti(IV) catalyst bearing a diimine ligand.

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Example 221

A 28-mg (0.046-mmol) sample of [(2,6-i-PrPh)₂DABMe₂]CoBr₂ was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.5 mL of polymethylalumoxane (3.3M) was injected, resulting in a deep purple solution, and the mixture was pressurized immediately with ethylene to 7 psig and stirred at 23°C for 17 hr. The solution remained deep purple but developed some viscosity due to polymer. The ethylene was vented; the offgas contained 1.5%

1-butene by gas chromatography (30-m Quadrex GSQ[®] Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl/methanol and was separated; concentration of the toluene solution yielded, after drying under high vacuum, 0.18g of elastomeric polyethylene. A film of polymer cast from chlorobenzene was stretchy with good elastic recovery. Differential scanning calorimetry: glass transition: -41°C; melting endotherm: 43°C (15J/g). This example demonstrates the efficacy of a cobalt (II) catalyst bearing a diimine ligand.

Example 222

A 35-mg (0.066-mmol) sample of [(2,6-i-PrPh)2DABMe2]FeCl2 was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the deep purple-blue solution became a royal purple solution, which evolved to deep green-black over time. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 70 hr, during which time the mixture became a pale green solution with black, sticky precipitate. The ethylene was vented; the toluene solution was

stirred with 6N HCl and methanol and was filtered to yield 90 mg of polyethylene.

Differential scanning calorimetry: melting endotherm: 128°C (84J/g). This example demonstrates the efficacy of a iron (II) catalyst bearing a diimine ligand.

Example 223

A mixture of 3.2g of the polyethylene product of Example 96, 60 mg (1.9 wt%) of dicumyl peroxide, and 50g (1.6 wt%) of triallylisocyanurate (TAIC) was 10 dissolved in 100 mL of THF. The polymer was precipitated by stirring the solution in a blender with water; the peroxide and TAIC are presumed to have stayed in the polymer. The polymer was pressed into a clear, rubbery, stretchy film at 125°C. Strips of this 15 film were subsequently pressed at various temperatures $(100^{\circ}\text{C}, 150^{\circ}\text{C}, 175^{\circ}\text{C}, 200^{\circ}\text{C})$ for various times (1 min, 5 min)min, 10 min) to effect peroxide-induced free-radical crosslinking. The cured sheets were all clear and stretchy and shorter-breaking: 100°C for 10 min gave no 20 apparent cure, while 150°C/5 min seemed optimal. cured films came closer to recovering their original dimensions than the uncured films. This example demonstrates peroxide curing of the amorphous elastomeric polyethylene. 25

Example 224

A 28-mg (0.050-mmol) sample of TiCl₄[2-NpCH=N(CH₂)₂N=CH-2-Np], where Np = naphthyl, (see structure below) was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the orange suspension became reddish-brown. The mixture was immediately pressurized with ethylene to 7 psig and was stirred at 23°C for 66 hr. The toluene solution was stirred with 6N HCl and methanol and was filtered to yield, after methanol washing and air-drying, 1.30g of white, fluffy polyethylene.

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Differential scanning calorimetry: melting endotherm: 135°C (242J/g).

This example demonstrates the efficacy of a catalyst with a bis-imine ligand in which the imine groups are not alpha to one another.

Example 225

A 33-mg (0.053-mmol) sample of [(2,6-i-10 PrPh)2DABMe2]ScCl3-THF was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the pale orange solution became 15 The mixture was immediately pressurized bright yellow. with ethylene to 7 psig and was stirred at 23°C for 17 hr, during which time the mixture remained yellow and granular suspended polymer appeared. The ethylene was vented; the toluene solution was stirred with 6N HCl 20 and methanol and was filtered to yield 2.77g of white, granular polyethylene. This example demonstrates the efficacy of a scandium (III) catalyst bearing a diimine ligand.

Example 226

25 <u>(2-t-BuPh) 2DABAN</u>

This compound was made by a procedure similar to that of Example 25. Three mL (19.2 mmol) of 2-t-butylaniline and 1.71 g (9.39 mmol) of acenaphthenequinone were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble). An orange product was crystallized from CH2Cl2 (3.51 g, 84.1%). 1H NMR (CDCl3, 250 MHz)d 7.85 (d, 2H, J = 8.0 Hz, BIAN: Hp), 7.52 (m, 2H, Ar: Hm), 7.35 (dd, 2H, J = 8.0, 7.3 Hz, BIAN: Hm), 7.21 (m, 4H,

Fig. Hm and Hp), 6.92 (m, 2H, Ar: Ho), 6.81 (d, 2H, J = 6.9 Hz, BIAN: Ho), 1.38 (s, 18H, C(CH3)3).

Example 227

Methyl vinyl ketone was stirred over anhydrous 5 K2CO3 and vacuum transferred on a high vacuum line to a dry flask containing phenothiazine (50 ppm). and methyl vinyl ketone (5 ml) were copolymerized according to Example 16 using catalyst {[(2,6-i-PrPh) 2DABMe2] PdCH2CH2CH2C(0)OCH3}+SbF6 (0.084 g, 0.10 mmol) to give 0.46 g copolymer (0.38 g after correcting for catalyst residue). $^{1}H-$ NMR (CDCl₃): 0.75-0.95(m, CH_3); 0.95-1.45(m, CH and CH_2); 1.55(m, - $CH_2CH_2C(0)CH_3$); 2.15(s, -CH₂CH₂C(0)CH₃); 2.4(t, -CH₂CH₂C(O)CH₃). Based on the triplet at 2.15, it 15 appears that much of the ketone functionality is located on the ends of hydrocarbon branches. Integration shows that the copolymer contains 2.1 mole% methyl vinyl ketone, and 94 methyl carbons (exclusive of methyl ketones) per 1000 methylene carbons. 20 turnover numbers are 128 equivalents of ethylene and 3 equivalents of methyl vinyl ketone per Pd. GPC (THF, PMMA standard): Mn=5360 Mw=7470 Mw/Mn = 1.39.

Example 228

A Schlenk flask containing 122 mg (0.0946 mmol) of 25 {[(4-MePh)₂DABMe₂]PdMe(N≡CMe)}+BAF was placed under a CO atmosphere. The yellow powder turned orange upon addition of CO, and subsequent addition of 20 mL of CH2Cl2 resulted in the formation of a clear red solution. t-Butylstyrene (10 mL) was added next and 30 the resulting orange solution was stirred for 25.7 h at room temperature. The solution was then added to methanol in order to precipitate the polymer, which was collected by filtration and dried in a vacuum oven at 50 °C overnight (yield = 4.03 g): GPC Analysis (THF, polystyrene standards): $M_w = 8,212$; $M_n = 4,603$; PDI = 35 1.78. The 1H NMR spectrum (CDCl3, 400 MHz) of the isolated polymer was consistent with a mixture of copolymer and poly(t-butylstyrene).

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Mixtures of alternating copolymer and poly(t-butylstyrene) were obtained from this and the following polymerizations and were separated by extraction of the homopolymer with petroleum ether. When R² and R⁵ were 4-MePh (this example) atactic alternating copolymer was isolated. When R² and R⁵ were 2,6-i-PrPh (Example 229) predominantly syndiotactic alternating copolymer was isolated. (Spectroscopic data for atactic, syndiotactic, and isotactic t-butylstyrene/CO alternating copolymers has been reported: M. Brookhart, et al., J. Am. Chem. Soc. 1992, 114, 5894-5895; M. Brookhart, et al., J. Am. Chem. Soc. 1994, 116, 3641-3642.)

Petroleum ether (~200 mL) was added to the polymer 15 mixture in order to extract the homopolymer, and the resulting suspension was stirred vigorously for several The suspension was allowed to settle, and the petroleum ether solution was decanted off of the gray powder. The powder was dissolved in CH2Cl2 and the 20 resulting solution was filtered through Celite. CH₂Cl₂ was then removed and the light gray powder (0.61 g) was dried in vacuo. ¹H and ¹³C NMR spectroscopic data are consistent with the isolation of atactic alternating copolymer: ${}^{1}H$ NMR (CDCl₃, 300 MHz) δ 7.6 -6.2 (br envelope, 4, Harvl), 4.05 and 3.91 (br, 1, CHAr'), 3.12 and 2.62 (br, 2, CH₂), 1.26-1.22 (br envelope, 9, CMe₃); 13 C NMR (CDCl₃, 75 MHz) δ 207.5 -206.0 (br envelope, -C(O)-), 150.0 - 149.0 (br, Ar': C_p), 135.0 - 133.8 (br envelope, Ar': C_{ipso}), 127.9 $(Ar': C_m)$, 126.0 - 125.0 (br, $Ar': C_o$), 53.0 - 51.0 (br envelope, CHAr'), 46.0 - 42.0 (br envelope, CH₂), 34.3 (CMe_3) , 31.3 (CMe_3) .

Example 229

The procedure of Example 228 was followed using 134 mg (0.102 mmol) {[(2,6-i-PrPh)_2DABMe_2]PdMe(N=CMe)}+BAF-. A mixture (2.47 g) of copolymer and poly(t-butylstyrene) was isolated. GPC Analysis (THF, polystyrene standards): $M_W=10,135$; $M_\Pi=4,922$; PDI =

2.06. Following the extraction of the homopolymer with petroleum ether, 0.49 g of off-white powder was ¹H and ¹³C NMR spectroscopic data are isolated. consistent with the isolation of predominantly syndiotactic copolymer, although minor resonances are present: ¹H NMR (CDCl₃, 300 MHz) δ 7.20 (d, 2, J = 8.14, Ar': H_o or H_m), 6.87 (d, 2, J = 7.94, Ar': H_o or (H_m) , 3.91 (dd, 1, J = 9.06, 3.16, CHAr'), 3.15 (dd, 1, J = 18.02, 9.96, CHH'), 2.65 (dd, 1, <math>J = 17.90, CHH'),10 1.25 (s, 9, CMe₃); 13 C NMR (CDCl₃, 75 MHz) δ 207.0 (-C(0) -), 149.8 (Ar': C_p), 134.5 (Ar': C_{ipso}), 127.8 (Ar': C_m), 125.6 (Ar': C_o), 51.7 (CHAr'), 45.6 (CH₂), 34.3 (CMe_3) , 31.3 (CMe_3) .

Example 230

- 15 A Schlenk flask containing 74.3 mg (0.0508 mmol) of {[(2,6-i-PrPh)₂DABMe₂]PdMe(OEt₂)}+BAF was evacuated, cooled to -78 °C and then placed under an atmosphere of ethylene/CO (1:1 mixture). Following the addition of 50 mL of chlorobenzene, the reaction mixture was 20 allowed to warm to room temperature and stirred. small amount of white precipitate appeared on the sides of the flask after 0.5 h and more precipitate formed during the next two days. After stirring for 47.2 h, the reaction mixture was added to methanol and the
- 25 resulting suspension was stirred. The precipitate was then allowed to settle, and the methanol was decanted, leaving behind a cream powder (0.68 g), which was dried in a vacuum oven at 70 °C for one day. 1 H and 13 C NMR spectroscopic data are consistent with the isolation of
- 30 an alternating copolymer of ethylene and carbon ¹H NMR (CDCl₃/pentafluorophenol, 400 MHz) δ monoxide: 2.89 $(-C(0)-CH_2CH_2-C(0)-)$; ¹³C NMR (CDCl₃/pentafluorophenol, 100 MHz) δ 212.1 (-C(0)-), 35.94 (CH₂).
- For comparisons of the spectroscopic data of 35 alternating E/CO copolymers herein with literature values, see for example: E. Drent, et al., J. Organomet. Chem. 1991, 417, 235-251.

Example 231

A Schlenk flask containing 73.2 mg (0.0500 mmol) of {[(2,6-i-PrPh)₂DABMe₂]PdMe(OEt₂)}+BAF⁻ was evacuated. cooled to -78 °C, and then back-filled with ethylene (1 atm). Chlorobenzene (50 mL) was added via syringe and the solution was allowed to warm to room temperature. After 0.5 h, the reaction vessel was very warm and ethylene was being rapidly consumed. The reaction flask was then placed in a room-temperature water bath and stirring was continued for a total of 3 h. A very viscous solution formed. The atmosphere was then switched to ethylene/carbon monoxide (1:1 mixture, 1 atm) and the reaction mixture was stirred for 47.7 more hours. During this time, the solution became slightly more viscous. The polymer was then precipitated by 15 adding the chlorobenzene solution to methanol. methanol was decanted off of the polymer, which was then partially dissolved in a mixture of Et₂O, CH₂Cl₂ and THF. The insoluble polymer fraction (2.71 g) was 20 collected on a sintered glass frit, washed with chloroform, and then dried in a vacuum oven at 70 °C for 12 h. The NMR spectroscopic data of the gray rubbery material are consistent with the formation of a diblock of branched polyethylene and linear 25 poly(ethylene-carbon monoxide): 1H NMR (CDCl $_3$ /pentafluorophenol, 400 MHz) δ 2.85 (-) $C(0) CH_2CH_2C(0) -$, 2.77 (- $C(0) CH_2$, minor), 1.24 (CH_2), 0.83 (CH₃); Polyethylene Block Branching: ~103 CH₃ per 1000 CH₂; Relative Block Length ((CH₂CH₂)_n-30 $(C(0)CH_2CH_2)_m$]: n/m = 2.0. ¹³C NMR (CDCl₃/pentafluorophenol, 100 MHz; data for ethylene-CO block) δ 211.6 (-C(0)-), 211.5 (-C(0)-, minor), 35.9

 $(C(0)-CH_2CH_2-C(0))$, 35.8 $(C(0)CH_2$, minor).

Example 232

A Schlenk flask containing 75.7 mg (0.0527 mmol) of {[(2,6-i-PrPh)2DABH2]PdMe(OEt2)}+BAF- was evacuated, cooled to -78 °C, and then back-filled with ethylene (1 atm). Chlorobenzene (50 mL) was added via syringe, the solution was allowed to warm to room temperature and stirred for 3 h. The solution did not become warm or viscous during this time. The atmosphere was changed to ethylene/carbon monoxide (1:1 mixture, 1 atm) and the solution was stirred for 47.7 more hours. 10 this time, the reaction mixture became quite viscous and solvent-swollen polymer precipitated on the sides of the flask. The polymer was precipitated by addition of the reaction mixture to methanol. The methanol was decanted off of the rubbery polymer (4.17 g), which was 15 then dried in a vacuum oven for one day at 70 °C. Chloroform was then added to the polymer and the rubbery insoluble fraction (0.80 g) was collected on a sintered glass frit. A 1H NMR spectrum (CDCl3, 400 20 MHz) of the chloroform-soluble polymer showed no carbon monoxide incorporation; only branched polyethylene was observed. NMR spectroscopic data for the chloroforminsoluble fraction was consistent with the formation of a diblock of branched polyethylene and linear 25 poly(ethylene-carbon monoxide): 1H NMR (CDCl₃/pentafluorophenol, 400 MHz) δ 2.88 $(C(0)CH_2CH_2C(0))$, 1.23 (CH_2) , 0.83 (CH_3) ; Polyethylene Block Branching: 132 CH3 per 1000 CH2; Relative Block Length [$(CH_2CH_2)_n - (C(0)CH_2CH_2)_m$]: n/m = 0.30; ¹³C NMR (CD₂Cl₂/pentafluorophenol, 100 MHz; data for ethylene-30 CO block) δ 211.3 (-C(O)-), 211.3 (-C(O)-, minor), 36.5 $(-C(0)CH_2CH_2C(0)-)$, 36.4 $(C(0)CH_2, minor)$.

Example 233

A 34-mg (0.053-mmol) sample of the crude product of Example 235, was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25 mL of dry, deaerated toluene. Then 0.6 mL of polymethylalumoxane (3.3M) was injected; the purple-pink suspension became a gold-

pressurized with ethylene to 152 kPa (absolute) and was stirred for 20 hr. Within the first hour, polymer was observed to be accumulating on the stir bar and the walls of the flask. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was filtered to yield (after MeOH and acetone washing and air-drying) 1.37g of white, granular polyethylene. This example demonstrates the efficacy of a catalyst with a 1,3-diimine ligand.

Example 234

Synthesis of MeC(=N-2.6-C6H3-iPr2)CH=C(NH-2.6-C6H3-iPr2)Me

Concentrated HCl (0.3 ml, 3.6 mmol) was added to a solution of 2,4-pentanedione (1.2 g, 12 mmol) and 2,6-15 diisopropylaniline (5.0 ml, 26.6 mmol) in 15 ml ethanol. The reaction mixture was refluxed for 21 h during which time a white solid precipitated. This was separated by filtration, dried under vacuum and 20 treated with saturated aqueous sodium bicarbonate. The product was extracted with methylene chloride, and the organic layer dried over anhydroùs sodium sulfate. Removal of the solvent afforded 1.43 g (28%) of the title compound as a white crystalline product; mp: 140-25 142° C; ¹H NMR: (CDCl₃) δ 12.12 (bs,1 H, NH), 7.12 (m, 6 H, aromatic), 4.84 (s, 1 H, C=CH-C), 3.10 (m, 4 H, isopropyl CH, J = 7 Hz), 1.72 (s, 6 H, CH₃), 1.22 (d, 12 H, isopropyl CH_3 , J = 7 Hz), 1.12 (d, 12 H, isopropyl CH₃, J = 7 Hz). ¹³C NMR: (CDCl₃) δ 161.36 30 (C=N), 142.63 (aromatic C-1), 140.89 (aromatic C-2), 125.27 (aromatic C-4), 123.21 (aromatic C-3), 93.41 (-CH=), 28.43 (isopropyl CH), 24.49 (isopropyl CH₃), 23.44 (isopropyl CH₃), 21.02 (CH₃). MS: m/z = 418.333(calc. 418.335).

Example 235

Synthesis of an ethylene polymerization catalyst from Ni (MeOCH₂CH₂OMe)Br₂ and MeC(=N-2.6-C₆H₃-iPr₂)CH=C(NH-2.6-C₆H₃-iPr₂)Me

Ni (MeOCH₂CH₂OMe)Br₂ (0.110 g, 0.356 mmol) and MeC(=N-2,6-C₆H₃-iPr₂)CH=C(NH-C₆H₃-iPr₂)Me (0.150 g, 0.359 mmol) were combined in 10 mL of methylene chloride to give a peach-colored suspension. The reaction mixture was stirred at room temperature overnight, during which time a lavender-colored powder precipitated. This was isolated by filtration, washed with petroleum ether and dried affording 0.173 g of material. This compound was used as the catalyst in Example 233.

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Example 236

[[(2,6-i-PrPh)2DABMe2]Pd(MeCN)2](BF4)2

[Pd(MeCN)4](BF4)2 (0.423 g, 0.952 mmol) and (2,6-i-PrPh)2DABMe2 (0.385 g, 0.951 mmol) were dissolved in 30 mL acetonitrile under nitrogen to give an orange solution. The reaction mixture was stirred at room temperature overnight; it was then concentrated in vacuo to afford a yellow powder. Recrystallization from methylene chloride/petroleum ether at -40°C afforded 0.63 g of the title compound as a yellow crystalline solid. 1H NMR (CD2Cl2) δ 7.51 (t, 2H, Hpara), 7.34 (d, 4H, Hmeta), 3.22 (sept, 4H, CHMe2), 2.52 (s, 6H, N=CMe), 1.95 (s, 6H, NC=Me), 1.49 (d, 12H, CHMe2), 1.31 (d, 12H, CHMe2).

Example 237

30 Ethylene Polymerization Catalyzed by {[(2,6-i-PrPh)2DABMe2]Pd(MeCN)2}(BF4)2

A 100 mL autoclave was charged with a solution of $\{[(2,6-i-PrPh)_2DABMe_2]Pd(MeCN)_2\}(BF_4)_2$ (0.043 g, 0.056 mmol) dissolved in 50 mL chloroform and ethylene (2.8 MPa). The reaction mixture was stirred under 2.8 MPa ethylene for 9 h 15 min. During this time, the temperature inside the reactor increased from 23 to $27^{\circ}C$. The ethylene pressure was then vented and

volatiles removed from the reaction mixture to afford 1.65 g of a viscous yellow oil. This was shown by ¹H NMR to be branched polyethylene containing 94 methylended branches per 1000 methylenes.

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Example 238

Ethylene polymerization by Ni(COD)₂/(2,6-i-PrPh)₂DABMe₂•HBAF(Et₂O)₂

Ni(COD)₂ (0.017 g, 0.06 mmol) and (2,6-i-PrPh)₂DABMe₂•HBAF(Et₂O)₂ (0.085 g, 0.06 mmol) were dissolved in 5 mL of benzene under nitrogen at room temperature. The resulting solution was quickly frozen, and then allowed to thaw under 6.9 MPa of ethylene at 50°C. The reaction mixture was agitated under these conditions for 18 h affording a solvent swelled polymer. Drying afforded 5.8 g of a polyethylene as a tough, rubbery material.

Example 239

Ethylene polymerization by Pd2(dba)3 (dba = dibenzylideneacetone)/(2.6-i-PrPh)2DABMe2•HBAF(Et20)2

- 20 A sample of (Et₂O) HBAF (200 mg, 0.20 mmol) was dissolved in 10 mL of Et₂O. To this solution was added 1 equivalent of DABMe₂ (or other α -diimine). The solution became red. Removal of the volatiles in vacuo gave a red solid of the acid- α -diimine complex.
- Pd2(dba)3 (0.054 g, 0.06 mmol) and (2,6-i-PrPh)2DABMe2•HBAF(Et2O)2 (0.076 g, 0.05 mmol) were dissolved in 5 mL of benzene under nitrogen at room temperature. The resulting solution was agitated under 6.9 MPa of ethylene at 50°C for 18 h. The product mixture was concentrated to dryness in vacuo, affording an extremely viscous oil. ¹H NMR showed the product to
 - an extremely viscous oil. ¹H NMR showed the product to be branched polyethylene containing 105 methyl ended branches per 1000 methylenes.

Example 240

Toluene (30 mL), 4-vinylcyclohexene (15 mL), and 20 mg of [(2,6-i-PrPh)2DABH2]NiBr2 (0.03 mmol) were combined in a Schlenk flask under an atmosphere of ethylene. A 10 % MAO solution (3 mL) in toluene was

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udded. The resulting purple solution was stirred for 16 h. After only a few hours, polymer began to precipitate and adhere to the walls of the flask. The polymerization was quenched and the polymer precipitated from acetone. The polymer was dried in vacuo overnight resulting in 100 mg of a white solid. Characterization by proton NMR suggests in corporation of 4-vinylcyclohexene as a comonomer. ^{1}H NMR (CDCl₃) δ 5.64 (m, vinyl, cyclohexene), 2.0-0.9 (overlapping m, including cyclohexyl methylene, methylene (PE), 10 methine), 0.78 (methyl, PE). There are also some minor signals in the base line that suggests incorporation of the internal olefin (cyclohexene) and free α -olefin (4vinyl).

15 Example 241

The catalyst {[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂CH₂C(O)OCH₃}SbF₆ (1.703 g, 2 mmol) was added to a 1 gal Hastalloy® autoclave. The autoclave was sealed, flushed with nitrogen and then charged with 1500 g of SO₂. An over pressure of 3.5 MPa of ethylene was maintained for 24 hr at 25°C. The autoclave was vented to relieve the pressure and the contents of the autoclave were transferred to a jar. The polymer was taken up in methylene chloride and purified by precipitation into excess acetone. The precipitated polymer was dried in vacuo to give 2.77 g of polymer. The polymer displayed strong bands attributable to sulfonyl group in the infrared (film on KBr plate) at 1160 and 1330 cm⁻¹.

Example 242

Copolymerizaton of Ethylene and Methyl Vinyl Ketone

Methyl vinyl ketone (MVK) was stirred over anhydrous K_2CO_3 and vacuum transferred using a high vacuum line to a dry flask containing phenothiazine (50 ppm). Ethylene and MVK (5 ml) were copolymerized using the procedure of Example 125 using as catalyst {[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3)SbF_6^- (0.084 g, 0.10)

Example 243

1-Hexene (20 ml) was polymerized in methylene 15 chloride (10 ml) according to example 173 to give 4.22 g of viscous gel (1002 equivalents 1-hexene per Pd). Integration of the ¹H NMR spectrum showed 95 methyl carbons per 1000 methylene carbons. 13C NMR quantitative analysis, branching per 1000 CH2: Total 20 methyls (103), Methyl (74.9), Ethyl (none detected), Propyl (none detected), Butyl (12.4), Amyl (none detected), ≥Hexyl and end of chains (18.1). Integration of the CH2 peaks due to the structure - $CH(R)CH_2CH(R')$, where R is an alkyl group, and R' is 25 an alkyl group with two or more carbons showed that in 74% of these structures, R = Me.

Listed below are the ^{13}C NMR data upon which the above analysis is based.

13c NMR data

TCB, 140C, 0.05M CrAcAc

Freq ppm	Intensity	
42.6359	4.05957	αα for Me & Et ⁺ branches
37.8987	9.10141	мв ₃ +
37.2833	64.4719	αB ₁
36.8537	8.67514	,
35.5381	4.48108	
34.8803	4.30359	
34.5514	5.20522	
34.2755	21.6482	
33.2411	4.13499	MB ₁
32.9811	32.0944	MB ₁
31.9467	14.0714	3B ₆ +, 3EOC
30.7212	5.48503	γ+γ+B, 3B ₄
30.2597	28.5961	γ+γ+B, 3B ₄
30.143	50.4726	γ+γ+B,3B ₄
29.7717	248	γ+γ+B,3B ₄
29.342	17.4732	γ+γ+B, 3B ₄
27.5702	27.2867	βy for 2 Me branches
27.1935	49.5612	$\beta\gamma+B$, (4B ₅ , etc.)
27.045	23.1776	
23.0292	9.56673	2B ₄
22.6526	14.1631	2B ₅ ⁺ , 2EOC
20.2495	5.72164	1B ₁
19.7455	48.8451	1B ₁
13.9049	21.5008	1B ₄ +, 1EOC

Example 244

1-Heptene (20 ml) was polymerized in methylene chloride (10 ml) according to example 173 to give 1.29 g of viscous gel (263 equivalents 1-heptene per Pd). Integration of the ¹H NMR spectrum showed 82 methyl carbons per 1000 methylene carbons. 13C NMR quantitative analysis, branching per 1000 CH2: Total 10 methyls (85), Methyl (58.5), Ethyl(none detected), Propyl (none detected), Butyl (none detected), Amyl (14.1), ≥Hexyl and end of chains (11.1). Integration of the CH_2 peaks due to the structure $-CH(R)CH_2CH(R')$ -, where R is an alkyl group, and R' is an alkyl group 15 with two or more carbons showed that in 71% of these structures, R = Me. DSC (two heats, -150-->150°C, 15° C/min) shows Tg = -42° C and a Tm = 28° C (45 J/g). Listed below are the 13C NMR data upon which the

above analysis is based.

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13_C NMR data

TCB, 120C, 0.05M CrAcAc

Freq ppm	Intensity	
42.6041	5.16375	aa for Me & Et+
37.851	15.9779	MB ₃ +
37.5963	7.67322	•
37.2356	99.6734	αBl
35.4956	7:58713	
34.8219	6.32649	
34.6097	6.37695	
34.2278	37.6181	
33.3418	3.78275	MB ₁
32.9228	60.7999	MB ₁
32.2809	13.6249	_
31.9148	21.2367	3B6+,3EOC
30.5886	13.8482	$\gamma + \gamma + B$, $3B_4$
30.4613	22.1996	γ+γ+B, 3B ₄
30.2173		γ+γ+B, 3B ₄
30.1059	80.2189	$\gamma+\gamma+B$, $3B_4$
29.7292	496	$\gamma + \gamma + B$, $3B_4$
29.3049		$\gamma + \gamma + B$, $3B_4$
27.1511	114.228	$\beta \gamma^{+}B_{1}$ (4B ₅ ,etc.)
27.0025	47.5199	• •
26.7267	20.4817	
24.5623	3.32234	
22.6207	36.4547	2B ₅ ⁺ , 2EOC
20.2176	7.99554	1B ₁
19.7084	70.3654	181
13.8677	36.1098	1B ₄ +, EOC

Example 245

1-Tetradecene (20 ml) was polymerized in methylene chloride (10 ml) according to example 173 to give 6.11 g of sticky solid (622 equivalents 1-tetradecene per Pd). Integration of the ¹H NMR spectrum showed 64 methyl carbons per 1000 methylene carbons. ¹³C NMR quantitative analysis, branching per 1000 CH2: Total methyls (66), Methyl (35.2), Ethyl(5.6), Propyl (1.2), Butyl (none detected), Amyl (2.1),

 \geq Hexyl and end of chains (22.8). Integration of the CH₂ peaks due to the structure -CH(R)CH₂CH(R')-, where R is an alkyl group, and R' is an alkyl group with two or more carbons showed that in 91% of these structures, R = Me. The region integrated for the structure where both R and R' are \geq Ethyl was 40.0 ppm to 41.9 ppm to avoid including a methine carbon

20 interference.

Listed below are the ¹³C NMR data upon which the above analysis is based.

13_C NMR data
TCB, 120C, 0.05M CrAcAc

Freq ppm	Intensity	
39.2826	6.684	MB ₂
37.8012	8.13042	MB3+
37.2171	24.8352	αB_1 , $3B_3$
34.1694	31.5295	$\alpha \gamma^{+}B$, $(4B_4,5B_5,$ etc.) MB_1
33.6809	13.0926	$\alpha\gamma^{+}B$, $(4B_4,5B_5,$ etc.) MB_1
32.9004	13.0253	MB ₁
31.9022	25.0187	3B ₆ +, 3EOC
30.1978	42.5593	γ+γ+B, 3B ₄
30.0969	34.1982	γ+γ+B, 3B ₄
29.7252	248	γ+γ+B, 3B ₄
29.3004	26.4627	γ+γ+B, 3B ₄
27.1394	31.8895	βγ+B,2B ₂ , (4B ₅ ,etc.)
26.9748	40.5922	$\beta\gamma+B,2B_2, (4B_5,etc.)$
26.3642	7.06865	$\beta\gamma+B,2B_2$, $(4B_5,etc.)$
22.6209	25.5043	2B ₅ ⁺ , 2EOC
19.6952	15.0868	1B ₁
137.8759	24.9075	1B ₄ +,1EOC
10.929	7.63831	1B ₂

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Example 246

This example demonstrates copolymerization of ethylene and 1-octene to give polymer with mostly C6+ branches. Under nitrogen, [(2,6-i-PrPh)2DABH2]NiBr2 (0.005 g, 0.0084 mmol) and 9.6 wt. % MAO in toluene 10 (0.50 mL) were dissolved in 10 mL of toluene at room temperature. The resulting solution was immediately transferred to a 100 mL autoclave that had previously been flushed with nitrogen and evacuated. 1-Octene (40 mL, 255 mmol) was then added to the reactor, which was 15 subsequently charged with ethylene (320 kPa). The reaction mixture was stirred for 60 min, during which time the temperature inside the reactor varied between 24 and 28°C. Ethylene was then vented, and the product polymer was precipitated by addition of the crude 20 reaction mixture to 50 mL of methanol containing 5 mL of concentrated aqueous HCl. The polymer precipitated as a slightly viscous oil; this was removed by pipette and dried affording 3.03 g of amorphous ethylene/1octene copolymer. Branching per 1000 CH2 was 25

juantified by ¹³C NMR ($C_6D_3Cl_3$, 25°C): total Methyls (83.6), Methyl (4), Ethyl(1.6), Propyl (4.4), Butyl (5.6), Amyl (10.1), \geq Hex and end of chains (65.8), \geq Am and end of chains (69.3), \geq Bu and end of chains (73.7). GPC (trichlorobenzene vs. linear polyethylene): $M_W = 48,200$, $M_D = 17,000$. DSC: $T_Q = -63$ °C.

Example 247

This example demonstrates copolymerization of ethylene and 1-octene to give polymer with mostly methyl and C6+ branches. Under nitrogen, [(2,6-i-10 PrPh) 2DABH2] NiBr2 (0.005 g, 0.0084 mmol) and 9.6 wt. % MAO in toluene (0.50 mL) were dissolved in 40 mL of toluene at -40°C. The resulting solution was immediately transferred to a 100 mL autoclave that had 15 previously been flushed with nitrogen and evacuated. 1-Octene (10 mL, 64 mmol) was then added to the reactor under 324 kPa of ethylene. The resulting reaction mixture was stirred under 324 kPa of ethylene for 1 h 10 min. During this time the temperature inside the 20 reactor varied between 29 and 40°C. Ethylene was then vented, and the product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 6.45 g of ethylene/1octene copolymer. Branching per 1000 CH2 was 25 quantified by 13 C NMR ($C_6D_3Cl_3$, 25° C): Total methyls (50.7), Methyl (13.7), Ethyl(2.4), Propyl (3.5), Butyl (4.1), Amyl (1), \geq Hex and end of chains (26), \geq Am and end of chains (30.4), ≥Bu and end of chains (31). (trichlorobenzene vs. linear polyethylene): $M_W =$ 30 $116,000, M_n = 9,570.$

Example 248

Under a nitrogen atmosphere, $Ni(COD)_2$ (0.017 g, 0.06 mmol) and $(2,6-i-PrPh)_2DABMe_2$ (0.024 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF (Et₂O)₂ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed

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to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C_2H_4 for 17.5 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 9.2 g. 1H NMR (CDCl₂CDCl₂, 120°C) showed that this sample contained 49 methyl-ended branches per 1000 methylenes. DSC: Tm = 118.8°C, $\Delta H_f = 87.0$ J/g.

Example 249

10 Under a nitrogen atmosphere, Ni[P(O-2-C6H4-Me)₃]₂(C_2H_4) (0.047 g, 0.06 mmol) and (2,6-i-PrPh) 2DABMe2 (0.024 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added $HBAF^{-}(Et_{2}O)_{2}$ (0.060 g, 0.06 mmol). The resulting 15 solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C₂H₄ for 18 h at ambient 20 temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 8.9 g. ¹H NMR (CDCl₂CDCl₂, 120°C) showed that this sample contained 47 methyl-ended branches per 1000 methylenes. DSC: Tm = 112.1°C, ΔH_f 25 = 57.5 J/q.

Example 250

A 100 mL autoclave was charged with a solution of Pd2(dba)3 (dba = dibenzylideneacetone) (0.054 g, 0.059 mmol) in 40 mL of chloroform. A solution of (2,6-i-30 PrPh)2DABMe2¥HBAF (Et2O)2 (0.085 g, 0.059 mmol) (see Example 256) in 10 mL of chloroform was then added under 2.1 MPa of ethylene. The reaction mixture was stirred for 3 h. During this time the temperature inside the reactor varied between 24 and 40°C.

35 Ethylene was then vented, and the product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 14.7 g of viscous polyethylene. ¹H NMR (CDCl3, 25°C) of this

material showed it to be branched polyethylene with 115 methyl-ended branches per 1000 methylenes. GPC analysis in trichlorobenzene gave $M_{\Pi}=97,300$, $M_{W}=225,000$ vs. linear polyethylene.

Example 251

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A 100 mL autoclave was charged with solid Pd(OAc)₂ (OAc = acetate) (0.027 g, 0.12 mmol) and (2,6-i-PrPh) 2DABMe2 (0.049 g, 0.12 mmol). The reactor was flushed with nitrogen and evacuated. A solution of 54 10 wt. % HBF4¥Et2O (0.098 g, 0.60 mmol) in 10 mL of chloroform was then added under 2.1 MPa of ethylene. The reaction mixture was stirred for 1.5 h. this time, the temperature inside the reactor varied between 24 and 37°C. Ethylene was then vented, and the 15 product polymer was precipitated by addition of the crude reaction mixture to methanol. The polymer was dried affording 4.00 g of viscous polyethylene. (CDCl₃, 25°C) of this material showed it to be branched polyethylene with 100 methyl-ended branches per 1000 20 methylenes. GPC analysis in trichlorobenzene gave M_n = 30,500, $M_W = 43,300$ vs. linear polyethylene.

Example 252

(Note: It is believed that in the following experiment, adventitious oxygen was present and acted as a cocatalyst.) Under nitrogen, {(2.6-i-PrPh)₂ DAB An]Ni(COD) (0.006 g, 0.009 mmol) and 9.6 wt. % MAO in toluene (0.54 mL, 1.66 mmol) were dissolved in 50 mL of toluene. This mixture was then transferred to a 100 mL autoclave. The autoclave was then charged with 2.1 MPa of ethylene. The reaction mixture was stirred for 8 min. During this time, the temperature inside the reactor varied between 23 and 51°C. Ethylene pressure was then vented. The product polymer was washed with methanol and dried, affording 8.44 g of polyethylene.

1H NMR (CDCl₂, 120°C) showed that this sample contained 77 methyl-ended branches per 1000 methylenes.

Example 253

Under nitrogen, [(2,4,6-MePh)DABAn]NiBr₂ (0.041 g, 0.065 mmol) was suspended in cyclopentene (43.95 g, 645 mmol). To this was added a 1 M solution of EtAlClo in toluene (3.2 mL, 3.2 mmol). The resulting reaction mixture was transferred to an autoclave, and under 700 kPa of nitrogen heated to 60°C. The reaction mixture was stirred at 60°C for 18 h; heating was then discontinued. When the reactor temperature had dropped to ~30°C, the reaction was quenched by addition of 10 isopropanol. The resulting mixture was stirred under nitrogen for several minutes. The mixture was then added under air to a 5 % aqueous HCl solution (200 mL). The precipitated product was filtered off, washed with acetone, and dried to afford 6.2 g of polycyclopentene 15 as a white powder. DSC of this material showed a broad melting transition centered at approximately 190°C and ending at approximately 250° C; Δ H_f = 18 J/g. gravimetric analysis of this sample showed a weight loss starting at 184°C: the sample lost 25% of its 20 weight between 184 and 470°C, and the remaining material decomposed between 470 and 500°C.

Example 254

Under nitrogen, [(2,6-Me-4-BrPh)₂DABMe₂]NiBr₂ (0.010 g, 0.015 mmol) was suspended in cyclopentene 25 (5.0 g, 73.4 mmol). To this was added a 1 M solution of EtAlCl₂ in toluene (0.75 mL, 0.75 mmol). resulting reaction mixture was stirred at room temperature for 92 h, during which time polycyclopentene precipitated. The reaction was then 30 quenched by addition of ~5 mL of methanol under nitrogen. Several drops of concentrated HCl was then added under air. The product was then filtered off, washed with more methanol followed by acetone, and dried to afford 1.31 q of polycyclopentene as a white powder. DSC of this material showed a broad melting 35 transition centered at approximately 200°C and ending at approximately 250° C; Δ Hf = 49 J/g. Thermal gravimetric analysis of this sample showed a weight

loss starting at -477° C; the sample completely decomposed between 477 and 507°C.

Example 255

Under nitrogen, [(2,6-i-PrPh),DABMe,]NiBr, (0.008 5 g, 0.015 mmol) was suspended in cyclopentene (5.00 g, 73.4 mmol). To this was added a 1 M solution of EtAlCl₂ in toluene (0.75 mL, 0.75 mmol). A magnetic stirbar was added to the reaction mixture and it was stirred at room temperature; after 92 h at room 10 temperature the reaction mixture could no longer be stirred due to precipitation of polycyclopentene At this point the reaction was then quenched by addition of ~5 mL of methanol under nitrogen. Several drops of concentrated HCl was then added under 15 The product was then filtered off, washed with more methanol followed by acetone, and dried to afford 2.75 g of polycyclopentene as a white powder. DSC of this material showed a broad melting transition centered at approximately 190°C and ending at approximately 250° C; $\Delta H_f = 34$ J/g. Thermal gravimetric 20 analysis of this sample showed a weight loss starting at ~480°C; the sample completely decomposed between 480 and 508°C.

Example 256

25 HBAF (0.776 mmol) was dissolved in 5 ml of Et₂O. A second solution of 0.776 mmol of $(2,6-i-PrPh)_2DABMe_2$ in 3 ml of Et₂O was added. The reaction turned deep red-brown immediately. After stirring for 2 h the volatiles were removed in vacuo to give the protonated α -diimine salt which was a red crystalline solid.

Example 257

HBF4 (0.5 mmol) was dissolved in 4 ml of Et₂O. A second solution of 0.5 mmol of $(2,6\text{-i-PrPh})_2DABMe_2$ in 3 ml of Et₂O was added. A color change to deep red occurred upon mixing. The reaction was stirred overnight. The volatiles were removed in vacuo to give to give the protonated α -diimine salt which was an orange solid.

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Example 258

HO₃SCF₃ (0.5 mmol) was dissolved in 4 ml of Et₂O. A second solution of 0.5 mmol of $(2,6-i-PrPh)_2DABMe_2$ in 3 ml of Et₂O was added. A color change to deep red occurred upon mixing after a few minutes an yellow-orange precipitate began to form. The reaction was stirred overnight. The product, believed to be the protonated α -diimine salt, was isolated by filtration rinsed with Et₂O and dried in vacuo.

10 Example 259

HBAF (0.478 mmol) was dissolved in 5 ml of Et₂O. A second solution of 0.776 mmol of [(2,6-i-PrPh)N=C(CH₃)]₂CH₂ in 3 ml of Et₂O was added. The reaction was stirred overnight. Removal of the volatiles in vacuo gave an off white solid, believed to be the protonated 1,3-diimine salt.

Example 260

HBF4 (0.478 mmol) was dissolved in 5 ml of Et₂O.

A second solution of 0.478 mmol of [(2,6-i-20 PrPh)N=C(CH₃)]₂CH₂ in 3 ml of Et₂O was added , the reaction turned cloudy with a white precipitate. The reaction was stirred overnight. The white solid, believed to be the protonated 1,3-diimine salt, was isolated by filtration rinsed with Et₂O and dried in vacuo.

Example 261

The product of Example 256 (78 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 140 kPa (absolute) of ethylene. A solution of 10 mg Ni(COD)₂ in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 157 mg of white spongy polyethylene.

Example 262

The product of Example 257 (27 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 35 kPa of ethylene. A solution of 10 mg Ni(COD)₂ in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 378 mg of sticky white polyethylene.

Example 263

The product of Example 258 (30 mg) was dissolved in 20 ml of toluene. The reaction vessel was charged with 140 kPa (absolute) of ethylene. A solution of 10 mg Ni(COD)₂ in 3 ml of toluene was added. Ethylene was added (138 kPa pressure, absolute) and the polymerization was run for 24 h at ambient temperature. Precipitation with MeOH gave 950 mg of amorphous polyethylene.

Example 264

To a burgundy slurry of 1 mmol of VCl₃ (THF)₃ in 10 20 ml of THF was added a yellow solution of 1 mmol of (2,6-i-PrPh)₂DABMe₂ in 4 ml of THF. After 10 minutes of stirring the reaction was a homogenous red solution. The solution was filtered to remove a few solids, concentrated and then cooled to -30°C. The red 25 crystals that formed were isolated by filtration, rinsed with pentane and dried in vacuo. The yield was 185 mg.

Example 265

The product of Example 264 (6 mg) was dissolved in 20 ml of toluene. The resulting solution was placed under 140 kPa (absolute) of ethylene. PMAO solution (0.8 mL, 9.6 wt% Al in toluene) was added and the polymerization was stirred for 3 h. The reaction was halted by the addition of 10% HCl/MeOH. The precipitated polymer was isolated by filtration, washed with MeOH and dried in vacuo. The yield was 1.58 g of white polyethylene.

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Example 266

Lanthanide metal tris-triflates (wherein the lanthanide metals were Y, La, Sm, Er, and Yb), 1 mmol, was slurried in 10 ml of CH₂Cl₂. A solution of 1 mmol of (2,6-i-PrPh)₂DABMe₂ in 3 ml of CH₂Cl₂ was added and the reaction stirred for 16 h at ambient temperature. The solution was filtered to give a clear filtrate. Removal of the solvent in vacuo gave light yellow to orange powders.

10 Example 267

Each of the various materials (0.02 mmol) prepared in Example 266 were dissolved in 20 ml of toluene. The resulting solutions were placed under 140 kPa (absolute) of ethylene. MMAO-3A solution (1.0 mL, 6.4 wt% Al in toluene) was added and the polymerizations were stirred for 3 h. The reactions were halted by the addition of 10% HCl/MeOH. The precipitated polymers were isolated by filtration washed with MeOH and dried in vacuo. Polymer yields are shown the following table,

	Lanthanide Metal	Yield (g)
	Yb	0.117
	La	0.139
	Sm	0.137
25	Y	0.139
	Er	0.167

Example 268

[(2,6-i-PrPh)₂DABMe₂]Ni-O₂ (68 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL, 9.6 wt.% Al in toluene) was added and the polymerization was conducted for 16 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 1.67 g of rubbery polyethylene.

Example 269

[(2,6-i-PrPh)₂DABMe₂]Ni-O₂ (65 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL, 9.6 wt.% Al in toluene) was added and the polymerization was conducted for 16 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 1.9 g of rubbery polyethylene.

Example 270

[(2,6-i-PrPh)₂DABMe₂]CrCl₂ (THF) (15 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 694 mg of polyethylene. DSC (-150 to 250°C at 10°C/min) results from the second heating were T_m 129°C, ΔH_f 204 J/g.

Example 271

[(2,6-i-PrPh)₂DABMe₂]CrCl₃ (14 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 833 mg of polyethylene. DSC (-150 to 250°C at 10°C/min) results from the second heating were T_m 133°C, ΔH_f 211 J/g.

Example 272

[(2,6-i-PrPh)₂DABMe₂]CrCl₂ (THF) (14 mg) was
dissolved in 20 ml of toluene. The reaction vessel was
placed under 138 kPa (absolute) of ethylene. MMAO-3A
(1 mL, 6.4 wt.% Al in toluene) was added and the
polymerization was conducted for 3 h. The reaction was

halted by the addition of 15 ml of 10% HCl/MeDH colution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 316 mg of polyethylene. DSC results from the second heating were (-150 to 250°C at 10° C/min) T_m 133°C, Δ Hf 107 J/g.

Example 273

[(2,6-i-PrPh)₂DABMe₂]CrCl₃ (15 mg) was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. MMAO-3A (1 mL, 6.4 wt.% Al in toluene) was added and the polymerization was conducted for 3 h. The reaction was halted by the addition of 15 ml of 10% HCl/MeOH solution. The precipitated polymer was isolated by

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solution. The precipitated polymer was isolated by filtration and dried under vacuum to yield 605 mg of polyethylene. DSC (-150 to 250°C at 10° C/min) results from the second heating were T_m 134°C, Δ H_f 157 J/g.

Example 274

A 61 mg sample of {[(2,6-i-PrPh)₂DABAn]Ni(η³-H₂CCHCHCl)]BAF was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried. The yield was 2.24 g of rubbery polyethylene.

Example 275

A 65 mg sample of $\{[(2,4,6\text{-MePh})_2\text{DABAn}]\text{Ni}(\eta^3\text{-H}_2\text{CCHCHCl})\}$ BAF was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried. The yield was 2.0 g of rubbery polyethylene.

Example 276

A 61 mg sample of $\{[(2,6-iPrPh)_2DABAn]Ni(\eta^3-H_2CCHCH_2)\}Cl$ was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of

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ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried. The yield was 1.83 g of rubbery polyethylene.

Example 277

A 60 mg sample of {[(2,6-iPrPh)₂DABMe₂]Ni(η³-H₂CCHCH₂)}Cl was dissolved in 20 ml of toluene. The reaction vessel was placed under 138 kPa (absolute) of ethylene. PMAO (0.7 mL) was added and the reaction stirred for 16 h. The polymerization was quenched by the addition of 15 ml of 10% HCl/MeOH. The polymer was isolated by filtration, washed with acetone and dried. The yield was 1.14 g of rubbery polyethylene.

Example 278

[(2,6-i-PrPh)2DAB(4-F-Ph)2]NiBr₂

In a 250-mL RB flask fitted with pressure equalizing addition funnel, thermometer, magnetic stirrer, and N₂ inlet was placed 0.75g (3.0mmol) of 4,4'-difluorobenzil, 13.8mL (80mmol) of 2,6-diisopropylaniline (DIPA), and 100mL dry benzene. In the addition funnel was placed 50mL of dry benzene and 2.0mL (3.5g; 18mmol) of titanium tetrachloride. The reaction flask was cooled to 2°C with ice and the TiCl4 solution was added dropwise over 45min, keeping the reaction temperature below 5°C. The ice bath was removed after addition was complete and the mixture was stirred at RT for 72h. The reaction mixture was partitioned between water and ethyl ether, and the ether phase was rotovapped and the concentrated oil was

washed with 800mL 1N HCl to remove the excess disopropylaniline. The mixture was extracted with 100mL of ether, and the ether layer was washed with water and rotovapped. Addition of 15mL hexane plus 30mL of methanol to the concentrate resulted in the formation of fine yellow crystals which were filtered, methanol-washed, and dried under suction to yield 0.4g of (2,6-i-PrPh) 2DAB(4-F-Ph) 2, mp: 155-158°C.

A 60-mg (0.092-mmol) sample of (2,6-i-PrPh)₂DAB(410 F-Ph)₂ was stirred under nitrogen with 32mg
(0.103mmol) of nickel(II) dibromide-dimethoxyethane
complex in 20mL of methylene chloride for 66h. The
orange-brown solution was rotovapped and held under
high vacuum for 2h to yield 86mg of red-brown solids.
15 The solid product was scraped from the sides of the
flask, stirred with 20mL hexane, and allowed to settle.
The yellow-orange hexane solution was pipetted off and
the remaining solid was held under high vacuum to yield
48mg of the orange-brown complex [(2,6-i-PrPh)₂DAB(4-F20 Ph)₂]NiBr₂.

Example 279

Ethylene polymerization with [(2,6-i-PrPh)₂DAB(4-F-Ph)₂]NiBr₂

A 26-mg (0.033-mmol) sample of [(2,6-i-PrPh) 2DAB (4-F-Ph) 2] NiBr2 was magnetically stirred under 25 nitrogen in a 50-mL Schlenk flask with 25mL of dry Then 0.6mL of polymethylalumoxane was injected, turning the orange-brown solution to a deep green- black solution. The mixture was pressurized immediately with ethylene to 152 kPa (absolute) and 30 stirred at RT for 17h. The reaction soon became warm to the touch; this heat evolution persisted for over an hour and the liquid volume in the Schlenk flask was observed to be slowly increasing. After 17h, the reaction was still dark green-brown, but thicker and 35 significantly (20%) increased in volume. The ethylene was vented; the offgas contained about 3% butenes (1butene, 1.9%; t-2-butene, 0.6%; c-2-butene, 0.9%) by GC

(30-m Quadrex GSQ Megabore column; 50-250°C at 10°/min). The toluene solution was stirred with 6N HCl/methanol and was separated; the toluene was rotovapped and held under high vacuum to yield 9.53g of low-melting polyethylene wax. There seemed to be significant low-boiling species present, probably low-mw ethylene oligomers, which continued to boil off under high vacuum. 1H NMR (CDCl3; 60°C) of the product showed a CH2:CH3 ratio of 206:17, which is 57 CH3's per 1000 CH2's. There were vinyl peaks at 5-5.8ppm; if the end groups are considered to be vinyls rather than internal olefins, the degree of polymerization was about 34.

Example 280

15 Synthesis of [(2-CF₃Ph)₂DABMe₂]NiBr₂

[(2-CF₃Ph)₂DABMe₂]NiBr₂

A mixture of 10.2mL (13.1g; 81.2mmol) 2aminobenzotrifluoride and 3.6mL (3.5g; 41mmol) freshly-20 distilled 2,3-butanedione in 15mL methanol containing 6 drops of 98% formic acid was stirred at 35°C under nitrogen for 8 days. The reaction mixture was rotovapped and the resultant crystalline solids (1.3g) were washed with carbon tetrachloride. The crystals 25 were dissolved in chloroform; the solution was passed through a short alumina column and evaporated to yield 1.0g of yellow crystals of the diimine (2-CF₃Ph)₂DABMe₂. ¹H NMR analysis (CDCl₃): 2.12ppm (s, 6H, CH3); 6.77 (d, 2H, ArH, J=9Hz); 7.20 (t, 2H, ArH, 30 J=7Hz); 7.53(t, 2H, ArH, J=7Hz); 7.68 (t, 2H, ArH,

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> J=8Hz). Infrared spectrum: 1706, 1651, 1603, 1579, 7.319, 1110cm⁻¹. Mp: 154-156°C.

A mixture of 0.207g (0.56mmol) of (2-CF₃Ph)₂DABMe₂ and 0.202g (0.65mmol) of nickel(II) dibromidedimethoxyethane complex in 13mL of methylene chloride was stirred at RT under nitrogen for 3hr. The redbrown suspension was rotovapped and held under high vacuum to yield 0.3g of [(2-CF₃Ph)₂DABMe₂]NiBr₂ complex.

Example 281

Ethylene polymerization with[(2-CF₃Ph)₂DABMe₂]NiBr₂ 10 A 13-mg (0.022-mmol) sample of [(2-CF₃Ph)₂DABMe₂]NiBr₂ was placed in a Parr® 600-mL stirred autoclave; 200mL of dry, deaerated hexane (dried over molecular sieves) was added and the hexane was saturated with ethylene by pressurizing to 450 kPa 15 (absolute) ethylene and venting. Then 1.0mL of modified methylalumoxane (1.7M in heptane; contains about 30% isobutyl groups) was injected into the autoclave with stirring, and the autoclave was stirred for 1hr under 690 kPa (absolute) ethylene as the 20 temperature rose from 20°C to 61°C over the first 20min and then slowly declined to 48°C by the end of the run. The ethylene was vented and 3mL of methanol was injected to stop polymerization; the autoclave contained a white suspension of fine particles of 25 polyethylene; the appearance was like latex paint. polymer suspension was added to methanol, and the polymer was stirred with MeOH/HCl to remove catalyst. The suspension was filtered and dried in a vacuum oven (75°C) to yield 26.8g of fine, white powdery 30 polyethylene Differential scanning calorimetry (15° C/min): Tg -45°C; mp 117°C (75J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): Mn=2,350; Mw=8,640; Mz=24,400;

Mw/Mn=3.67. A solution of the polymer in chlorobenzene

could be cast into a waxy film with little strength.

Example 282

Under nitrogen, Ni(COD)₂ (0.017 g, 0.062 mmol) and (2,4,6-MePh)₂DABAn (0.026 g, 0.062 mmol) were dissolved in 2.00 g of cyclopentene to give a purple solution. The solution was then exposed to air (oxygen) for several seconds. The resulting dark red-brown solution was then put back under nitrogen, and EtAlCl2 (1 M solution in toluene, 3.0 mL, 3.0 mmol) added. A cranberry-red solution formed instantly. The reaction mixture was stirred at room temperature for 3 days, 10 during which time polycyclopentene precipitated. reaction was then quenched by the addition of methanol followed by several drops of concentrated HCl. reaction mixture was filtered, and the product polymer 15 washed with methanol and dried to afford 0.92 g of polycyclopentene as an off-white powder. gravimetric analysis of this sample showed a weight loss starting at 141°C: the sample lost 18% of its weight between 141 and 470°C, and the remaining material decomposed between 470 and 496°C. 20

Example 283

Under a nitrogen atmosphere, Ni(COD)₂ (0.017 g, 0.06 mmol) and the ligand shown below (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF (Et₂O)₂ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C₂H₄ for 18 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 11.0 g.

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Example 284

The catalyst {[(2,6-i-

 $PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3$ *SbF₆ (0.025g, 0.03 5 mmol) and $CH_2=CH(CH_2)_6C_{10}F_{21}$ (4.74g, 7.52 mmol) were dissolved in 20 mL CH2Cl2 in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT 10 under 1 atm of ethylene for 72 hr. Solvent was evaporated to almost dryness. Acetone (70 mL) was added and the mixture was stirred vigorously overnight. The upper layer was decanted. The resulting yellow solid was washed with 3x15 mL acetone, vacuum dried, 15 and 1.15g of product was obtained. ¹H NMR analysis (CD₂Cl₂): 105 methyls per 1000 methylene carbons. Comparison of the integral of the $CH_2R_f(2.10 \text{ ppm})$ with the integrals of methyls(0.8-1.0 ppm) and methylenes(1.2-1.4 ppm) indicated a comonomer content 20 of 6.9 mol%. The polymer exhibited a glass transition temperature of -55°C(13J/g) and a melting point of 57°C by differential scanning calorimetry. Gel permeation

chromatography (THF, polystyrene standard): Mw = 39,500, Mn = 34,400, P/D = 1.15.

Example 285

In a 100 mL Schlenk flask, [(2,6-i-PrPh)₂DABAn]NiBr₂ (0.012g, 0.017mmol) and CH₂=CH(CH₂)₆C₁₀F₂₁ (4.62g, 7.33 mmol) were dissolved in 32 mL of toluene under stirring. This was pressured with 1 atm ethylene and was allowed to stir at 0°C for 15 minutes. MAO (1.7 mL, 8.9 wt% in toluene) was added. This was allowed to vigorously stir at RT for

30 min. Sixty mL methanol was then added. The white rolid was filtered, followed by 3x30 ml 3:1 methanol/toluene wash, vacuum dried, and 3.24g of white polymer was obtained. ¹H NMR analysis (o-

dichlorobenzene- d_4 ,135 $^{\circ}$ C): 64 methyls per 1000 methylene carbons. Comparison of the integral of the CH_2R_f (2.37ppm) with the integrals of methyls (1.1-1.2 ppm) and methylenes (1.4-1.8 ppm) indicated a comonomer content of 8.7 mol%. Mw = 281,157, Mn = 68,525, P/D =

10 4.1.

Example 286

In a 100 mL Schlenk flask, [(2,6-i-PrPh)₂DABAn]NiBr₂ (0.012g, 0.017mmol) and CH₂=CH(CH₂)₆C₁₀F₂₁ (4.62g, 7.33 mmol) were dissolved in 32 mL of toluene under stirring. This was allowed to stir at 0 °C for 15 minutes. MAO (1.7 mL, 8.9 wt% in toluene) was added. This was allowed to stir at 0°C for 2.5 h and then RT for 3 h. Methanol (200 mL) was then added, followed by 1 mL conc. HCl. The white solid was filtered and washed with methanol, vacuum dried, and 0.79g of white solid polymer was obtained. By differential scanning calorimetry, Tm 85°C(22J/g).

Example 287

 $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(0)OCH_3\}^*SbF_6^*\}$ (0.0205g, 0.024 mmol) and $CH_2=CH(CH_2)_4(CF_2)_4O(CF_2)_2SO_2F$ 25 (3.5g, 7.26 mmol) were dissolved in 18 mL CH₂Cl₂ in a The flask was connected to Schlenk flask in a drybox. a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. was stirred at RT under 1 atm of ethylene for 72 hr. 30 Solvent was evaporated after filtration. The viscous oil was dissolved in 10 mL CH2Cl2, followed by addition of 100 mL methanol. The upper layer was decanted. reverse precipitation was repeated two more time, followed by vacuum drying to yield 3.68g of a light 35 yellow viscous oil. H NMR analysis (CDCl3): methyls per 1000 methylene carbons. Comparison of the integral of the CH_2CF_2 - (2.02 ppm) with the integrals

of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm)
indicated a comonomer content of 8.5 mol%. ¹⁹F NMR
(CDCl₃): 45.27 ppm, -SO₂F; -82.56 ppm, -83.66 ppm, 112.82 ppm, -115.34 ppm, -124.45 ppm, -125.85 ppm, CF₂

peaks. The polymer exhibited a glass transition
temperature of -57 °C by differential scanning
calorimetry. Gel permeation chromatography (THF,
polystyrene standard): Mw = 120,000, Mn = 78,900, P/D
= 1.54. The turnover numbers for ethylene and the
comonomer are 2098 and 195, respectively.

Example 288

In a 100 mL Schlenk flask, [(2,6-i-PrPh)₂DABAn]NiBr₂ (0.017g, 0.024 mmol) and CH₂=CH(CH₂)₄(CF₂)₄O(CF₂)₂SO₂F (5.0g, 10 mmol) were dissolved in 25 mL of toluene under stirring. MAO (2.3 mL, 8.9 wt% in toluene) was added. This was allowed to stir at RT for 15 hr. Sixty mL methanol was then added, followed by 1 mL conc. HCl. The upper layer was decanted, residue washed with methanol (5x5 mL), vacuum dried, and 1.20g of a white viscous oil was obtained. ¹⁹F NMR (Hexafluorobenzene, 80 °C): 45.20 ppm, -SO₂F; -81.99 ppm, -82.97 ppm, -112.00 ppm, -114.36 ppm, -123.60 ppm, -124.88 ppm, CF₂ peaks.

Example 289

In a Schlenk flask, [(2,6-i-PrPh)2DABAn]NiBr2 25 (0.012g, 0.017mmol) and $CH_2=CH(CH_2)_4(CF_2)_4O(CF_2)_2SO_2F$ (3.26g, 6.77mmol) were dissolved in 35 mL of toluene under stirring. This was pressured with 1 atm ethylene and was allowed to stir at 0° C for 15 minutes. (1.7 mL, 8.9 wt% in toluene) was added. 30 allowed to vigorously stir at RT for 45 minutes. Methanol (140 mL) was then added, followed by addition of 1 mL of conc. HCl. The white solid was filtered, followed by methanol wash, vacuum dried to obtain 2.76g of a white rubbery polymer. ¹H NMR analysis (o-35 dichlorobenzene- d_4 , 100 °C): 98 methyls per 1000 methylene carbons. Comparison of the integral of the - CH_2CF_2 - (2.02 ppm) with the integrals of methyls (0.8-

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1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 3.5 mol%. ¹⁹F NMR ((0-dichlorobenzene- d_4): 45.19 ppm, -SO₂F; -82.70 ppm, -83.72 ppm, -112.96 ppm, -115.09 ppm, -124.37 ppm, -125.83 ppm, CF_2 peaks. The polymer exhibited Tm of 97°C by differential scanning calorimetry. Mw = 156,000, Mn = 90,000, P/D = 1.73.

Example 290

 $\{ [(2,6-i-PrPh)_2DABMe_2] PdCH_2CH_2CH_2C(0)OCH_3 \}^*SbF_6^-$ (0.030g, 0.035 mmol) and $CH_2=CH(CH_2)_4(CF_2)_2CO_2Et$ (3.0g, 10 11.7 mmol) were dissolved in 20 mL CH₂Cl₂ in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. was stirred at RT under 1 atm of ethylene for 72 h. 15 Solvent was evaporated. The viscous oil was dissolved in 10 mL acetone, followed by addition of 60 mL methanol. The mixture was centrifuged. layer was decanted. The oil was dissolved in 10 mL acetone followed by addition of 60 mL methanol. 20 mixture was centrifuged again. The viscous oil was collected, and vacuum dried to obtain 1.50g of a light yellow viscous oil. ¹H NMR analysis (CDCl₃): 67 methyls per 1000 methylene carbons. Comparison of the integral of the CH_2CF_2 - (2.02 ppm) with the integrals 25 of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 11 mol%. The polymer exhibited a Tg of -61°C by DSC. GPC (THF, polystyrene standard): Mw = 73,800, Mn = 50,500, P/D = 1.46.

Example 291

In a Schlenk flask, $[(2,6-i-PrPh)_2DABAn]NiBr_2$ (0.019g, 0.026 mmol) and $CH_2=CH(CH_2)_4(CF_2)_2CO_2Et$ (3.0g, 11.7 mmol) were dissolved in 35 mL of toluene. This was placed under 1 atm of ethylene at 0°C for 15 minutes. MAO (2.6 mL, 8.9 wt% in toluene) was added. This was allowed to vigorously stir at 0°C for 30 minutes. Methanol (120 mL) was then added, followed by 1 mL conc. HCl. The solid was filtered, washed with

methanol and hexane, and vacuum dried to yield 1.21g of white rubbery solid. ¹H NMR analysis (TCE-d₂, 110°C): Comparison of the integral of the CH₂CF₂- (2.06 ppm) with the integrals of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 6.0 mol%. The polymer exhibited a Tg of -46°C and Tm's at 40°C and 82°C by DSC.

Example 292

In a Schlenk flask, [(2,6-i-PrPh)2DABAn]NiBr2 (0.022g, 0.030 mmol) and $CH_2=CH(CH_2)_4(CF_2)_2CO_2Et$ (3.5g, 10 13.7 mmol) were dissolved in 30 mL of toluene. was placed under nitrogen at 0°C for 15 minutes. MAO (3.0 mL, 8.9 wt% in toluene) was added. allowed to stir at 0°C for 2.5 h and then RT for 6 h. Fifty mL methanol was then added, followed by 1 mL 15 conc. HCl. The mixture was washed with 3x60 mL water. The organic layer was isolated and dried by using Na₂SO₄. Evaporation of toluene and addition of hexane resulted in precipitation of an oil. The oil was washed with hexane another two times, and vacuum dried 20 to yield 0.16g of a yellow oil. Mw = 35,600, Mn = 14,400, P/D = 2.47.

Example 293

 $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2C(0)OCH_3\}^*SbF_6^*\}$ (0.0848g, 0.1 mmol) and $CH_2=CH(CH_2)_4(CF_2)_2O(CF_2)_2SO_2F$ 25 (11.5g, 0.03 mol) were dissolved in 72 mL CH_2Cl_2 in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. was stirred at RT under 1 atm of ethylene for 72 hr. 30 The solution was filtered through Celite and then concentrated to 70 mL. Methanol (400 mL) was added under stirring. The upper layer was decanted. was redissolved in 70 mL CH2Cl2 followed by addition of 350 mL methanol. The viscous oil was collected, vacuum 35 dried and 24.1g of a light yellow viscous oil was obtained. H NMR analysis (CDCl₃): 113 methyls per 1000 methylene carbons. Comparison of the integral of

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the CH_2CF_2 - (2.0 ppm) with the integrals of mathyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 2.9 mol%. The polymer exhibited a Tg of -66°C by DSC. GPC (THF, polystyrene standard): Mw = 186,000, Mn = 90,500, P/D = 2.06. The turnover numbers for ethylene and the comonomer are 6,122 and 183, respectively.

Examples 294-300

All of these Examples were done under 1 atm ethylene with a MA concentration of 1.2M and 10 {[(diimine)PdMe(Et₂O)] *SbF₆) concentration of 0.0022M at RT for 72 hr. Results are shown in the Table below.

Ex.	Diimine	MA (mol%) *	Mn	P/D
NO. 294	(2,6-i-	6	12,300	1.8
234	PrPh) 2DABMe2	,	,	
295	(2,6-EtPh) ₂ DABMe ₂	16	7,430	1.9
296	(2,4,6-	23	2,840	2.1
	MePh) 2DABMe2			
297	$(2,4,6-MePh)_2DABAn$	37	1,390	14
298	$(2,4,6-MePh)_2DABH_2$	46	1,090	3.1
299	(2-i-PrPh) ₂ DABMe ₂	17	410	**
300	(2-MePh) ₂ DABMe ₂	29	320	**

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Example 301

 $\{[(2,6-EtPh)_2DABMe_2]PdCH_3(Et_2O)\}^*SbF_6$ (0.0778g, 0.10 mmol) and methyl acrylate (4.78g, 0.056 mol) were dissolved in 40 mL CH2Cl2 in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT 25 under 1 atm of ethylene for 72 h. The mixture was filtered through silica gel, solvent was evaporated and then vacuum dried, and 1.92g light of a yellow viscous oil was obtained. ¹H NMR analysis (CDCl₃): 69 methyls per 1000 methylene carbons. Comparison of the integral 30

In the polymer

Mn characterized by 'H NMR.

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of the methyl on the ester groups (2.3 ppm) with the integrals of carbon chain methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 16 mol%. The polymer exhibited a Tg of -68° C by DSC. GPC (THF, polystyrene standard): Mw = 14,300, Mn = 7,430, P/D = 1.93.

Example 302

 $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}^*SbF_6^-\}$ (0.254g, 0.30 mmol) and $CH_2=CHCO_2CH_2(CF_2)_6CF_3$ (90.2g, 0.20 mol) were dissolved in 150 mL CH₂Cl₂ in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 24 h. The solution was decanted to 1200 mL methanol, resulted formation of oil at the bottom of the flask. The upper layer was decanted, oil dissolved in 150 mL CH2Cl2, followed by addition of 1200 mL of methanol. The upper layer was decanted, oil dissolved in 600 mL hexane and filtered through Celite®. Solvent was evaporated, and then vacuum dried, yielding 54.7g of a viscous oil. 1H NMR analysis (CDCl₃): 99 methyls per 1000 methylene carbons. Comparison of the integral of the CH2CF2-(4.56 ppm) with the integrals of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 5.5 mol%. The polymer exhibited a Tg of - 49° C by DSC. Mw = 131,000, Mn = 81,800.

Example 303

{[(2,6-i-PrPh)₂DABMe₂]PdCH₂CH₂C(O)OCH₃}*SbF₆

(0.169g, 0.20 mmol) and β-hydroxyethyl acrylate (6.67g, 0.057 mol) were dissolved in 40 mL CH₂Cl₂ in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 45 h. Solvent was evaporated. The residue was dissolved in 100 mL hexane, followed by addition of 400 mL methanol. Upon standing overnight, a second upper layer formed and was

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The oil was dissolved in 60 mL THF, tollowed by addition of 300 mL water. The upper layer was The residue was dissolved in 100 mL 1:1 This was filtered through Celite®. The $CH_2Cl_2/hexane$. solvent was evaporated, vacuum dried and 6.13g of a light yellow oil was obtained. 1H NMR analysis (CD₂Cl₂): 142 methyls per 1000 methylene carbons. Comparison of the integral of the CH₂CO₂- (2.30 ppm) with the integrals of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content 10 of 2.6 mol%. Mw = 53,100, Mn = 37,900, P/D = 1.40.

Example 304

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 $\{[(2,6-i-PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3\}^*SbF_6^-\}$ (0.169g, 0.20 mmol) and hydroxypropyl acrylate (7.52g, 0.058 mol) were dissolved in 40 mL CH₂Cl₂ in a flask in the drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred at RT under 1 atm of ethylene for 72 h. Solvent was evaporated. Eighty mL methanol was added to dissolve the residue, followed by 250 mL water. The upper layer was decanted. The reverse precipitation was repeated one more time. The oil was isolated, vacuum dried, and 1.1g of a light yellow oil was obtained. ¹H NMR analysis (CD₂Cl₂): 94 methyls per 1000 methylene carbons. Comparison of the integral of the CH2CO2-(2.30 ppm) with the integrals of methyls(0.8-1.0 ppm) and methylenes(1.1-1.4 ppm) indicated a comonomer content of 6.5 mol%. Mw = 39,200, Mn = 28,400, P/D =30 1.38.

Example 305

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed into a glass vial in the dry box (0.0141 g, 0.025 Cyclopentene was added (3.41 g, 2,000 equivalents/Ni). A solution of MMAO (Akzo Nobel MMAO-3A, modified methylaluminoxane, 25% isobutyl groups in place of methyl groups) was added while stirring (0.75 ml, 1.7 M Al in heptane, 50 equivalents/Ni). Following

addition of the MMAO, the solution was homogeneous. After stirring for several hours, solid polymer started to precipitate. After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.66 g polymer (388 turnovers/Ni). The polymer was pressed at 292°C to give a transparent, light gray, tough film. DSC (25 to 300°C, 15°C/min, second heat): Tg = 104°C, Tm (onset) = 210°C, Tm (end) = 285;C, Heat of fusion = 14 J/g. X-ray powder diffraction shows peaks at d-spacings 5.12, 4.60, 4.20, 3.67, and 2.22. 1H NMR (500 MHz, 155°C, d4-o-dichlorobenzene, referenced to downfield peak of solvent = 7.280 ppm): 0.923 (bs, 1.0 H, -CHC $\underline{\text{H}}_2$ CH-); 1.332 (bs, 2.0 H, - $CHCH_2CH_2CH_-$); 1.759 (bs, 4.0 H, $-CHCH_2CH_2CH_-$ and - $CHCH_2CH_2CH_-$); 1.947 (bs, 1.0 H, -CHCH₂CH-). assignments are based upon relative integrals and 1H -13C correlations determined by 2D NMR. This spectrum is consistent with an addition polymer with cis-1,3 enchainment of the cyclopentene.

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Example 306

Cyclopentene was polymerized by [(2,4,6-MePh) 2DABMe2] PdMeCl and MMAO according to Example 305 to give 0.37 g polymer (217 turnovers/Pd). The polymer 25 was pressed at 250°C to give a transparent, light brown, tough film. DSC (25 to 300°C, 15°C/min, second heat): Tg = 84°C, Tm(onset) = 175°C, Tm(end) = 255°C, Heat of fusion = 14 J/g. 1 H NMR (400 MHz, 120°C, d_4 -odichlorobenzene, referenced to downfield peak of 30 solvent = 7.280 ppm): 0.90 (bs, 1 H, -CHCH2CH-); 1.32 (bs, 2 H, -CHCH₂CH₂CH-); 1.72, 1.76 (bs, bs 4 H, - $CHCH_2CH_2CH$ and $-CHCH_2CH_2CH$); 1.94 (bs, 1 H, $-CHCH_2CH$ -The assignments are based upon relative integrals and ¹H - ¹³C correlations determined by ²D NMR. 35 spectrum is consistent with an addition polymer with cis-1,3 enchainment of the cyclopentene.

Example 307

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Cyclopentene was polymerized by [(2,62-FtPh) 2DABMe2] PdMeCl and MMAO according to Example 305 to give 0.39 g polymer (229 turnovers/Pd). The polymer was pressed at 250°C to give a transparent, light brown, tough film. DSC (25 to 300°C, 15°C/min, second heat): $Tq = 88^{\circ}C$, $Tm(onset) = 175^{\circ}C$, $Tm(end) = 255^{\circ}C$, Heat of fusion = 16 J/q. 1 H NMR (300 MHz, 120°C, d_4 -odichlorobenzene) is very similar to the spectrum of Example 306.

Example 308 10

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Cyclopentene was polymerized by [(2,4,6-MePh) 2DABMe2] NiBr2 and MMAO according to Example 305 to give 0.36 g polymer (211 turnovers/Ni). The polymer was pressed at 250°C to give a transparent, colorless, tough film. DSC (25 to 300°C, 15°C/min, second heat): Tq = 98°C, Tm(onset) = 160°C, Tm(end) = 260°C, Heat of fusion = 22 J/g. 1 H NMR (500 MHz, 120 $^{\circ}$ C, d_{4} -odichlorobenzene) is very similar to the spectrum of Example 306. X-ray powder diffraction shows the same crystalline phase as observed in Example 305. 20

Example 309

Cyclopentene was polymerized by [(2,6-i-PrPh) 2DABMe2] PdMeCl and MMAO according to Example 305 to give 0.73 g of fine powder (429 turnovers/Pd). polymer was pressed at 250°C to give a transparent, light brown tough film. DSC (25 to 300°C, 15°C/min, second heat): Tg = 96°C, Tm(onset) = 175°C, Tm (end) = 250°C, Heat of fusion = 14 J/g. 1 H NMR (400 MHz, 120°C, d₄-o-dichlorobenzene) is very similar to the spectrum of Example 306. X-ray powder diffraction shows the same crystalline phase as observed in Example 305.

Example 310

Cyclopentene was polymerized by [(2,6-i-PrPh)2DABMe2]PdCl2 and MMAO according to Example 305 to give 0.856 g polymer (503 turnovers/Pd). The polymer was pressed at 250°C to give a transparent, light brown, tough film. DSC (25 to 300°C, 15°C/min, second heat): Tg = 104°C, Tm(onset) = 140°C, Tm(end) = 245°C,

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Heat of fusion = 19 J/g. 1 H NMR (400 MHz, 120°C, d_4 -odichlorobenzene) is very similar to the spectrum of Example 306.

Example 311

Cyclopentene was polymerized by [(2,6-EtPh) 2DABMe2] NiBr2 and MMAO according to Example 305 to give 0.076 g polymer (45 turnovers/Ni). ¹H NMR (400 MHz, 120°C, d₄-o-dichlorobenzene) is very similar to the spectrum of Example 306.

Example 312

Heat of fusion = 35 J/g.

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10 Cyclopentene was polymerized by [(2,4,6-MePh) 2DABH2] NiBr2 and MMAO according to Example 305 to give 0.66 g polymer (388 turnovers/Ni). The polymer was pressed at 292°C to give a tough film. 1H NMR (400 MHz, 120°C, d₄-o-dichlorobenzene) is very similar to 15 the spectrum of Example 306. A DSC thermal fractionation experiment was done in which a sample was heated to 330°C at 20°C/minute followed by stepwise isothermal equilibration at the followed temperatures (times): 280°C (6 hours), 270°C (6 hours), 260°C (6 20 hours), 250°C (6 hours), 240°C (4 hours), 230°C (4 hours), 220°C (4 hours), 210°C (4 hours), 200°C (3 hours), 190°C (3 hours), 180°C (3 hours), 170°C (3 hours), 160°C (3 hours), 150°C (3 hours). The DSC of this sample was then recorded from 0°C - 330°C at 10° 25 $Tg = 98^{\circ}C$, $Tm (onset) = 185^{\circ}C$, $Tm (end) = 310^{\circ}C$,

Example 313

Cyclopentene was polymerized by [(2-PhPh) 2DABMe2] NiBr2 and MMAO according to Example 305 to 30 give 1.24 g polymer (728 turnovers/Ni). The polymer was pressed at 292°C to give a transparent, light gray, brittle film. DSC (25 to 320°C, 10°C/min, second heat): Tm(onset) = 160°C, Tm (end) = 285°C, Heat of fusion = 33 J/g. ^{1}H NMR (400 MHz, 120°C, d_{4} -o-35 dichlorobenzene) is very similar to the spectrum of Example 306. Several peaks attributed to cyclopentenyl end groups were observed in the range 5.2-5.7 ppm.

Integration of these peaks was used to calculate $M_n=130$. IR (pressed film, cm⁻¹): 3050 (vw, olefinic end group, CH stretch), 1615(vw, olefinic end group, cis-CH=CH- double bond stretch), 1463(vs), 1445(vs), 1362(s), 1332(s), 1306(s), 1253(m), 1128(w), 1041(w), 935(m), 895(w), 882(w), 792(w), 721(w, olefinic end group, cis-CH=CH-, CH bend). GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run at 100°C in tetrachloroethylene, polystyrene calibration): Peak MW = 13,900; $M_n=10,300$; $M_w=17,600$; $M_w/M_n=1.70$.

Example 314

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The complex $[(2,4,6\text{-MePh})_2\text{DABAn}]$ NiBr₂ was weighed into a glass vial in the dry box (0.032~g,~0.050~mmol). Toluene (2.35~ml) and cyclopentene (6.81~g,~2,000) equivalents/Ni) were added, followed by $C_6H_5\text{NHMe}_2^+$ $B(C_6F_5)_4^-$ (0.04~g,~50~equivalents/Ni). A solution of Et₃Al was added while stirring (2.5~ml,~1~M~in heptane,50~equivalents/Ni). After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.16 g of fine powder (47~turnovers/Ni). A control experiment with no $C_6H_5\text{NHMe}_2^+$ $B(C_6F_5)_4^-$ gave no polymer.

Example 315

The complex [(2,4,6-MePh)₂DABAn]NiBr₂ was weighed into a glass vial in the dry box (0.032 g, 0.050 mmol). Toluene (3.46 ml) and cyclopentene (6.81 g, 2,000 equivalents/Ni) were added. A solution of Et₂AlCl was added while stirring (1.39 ml, 1.8 M in toluene, 50 equivalents/Ni). After stirring for 46 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 0.53 g of fine powder (156 turnovers/Ni).

Example 316

The complex $[(2,4,6-MePh)_2DABMe_2]NiBr_2$ was weighed into a glass vial in the dry box $(0.0070 \text{ g},\ 0.0130$

Pentane (2.2 ml) and cyclopentene (10.0 g, 11,300 equivalents/Ni) were added. A solution of EtAlCl₂ was added while stirring (0.73 ml, 1.0 M in hexanes, 56 equivalents/Ni). After stirring for 192 hours, the solution was filtered and the solids were washed several times on the filter with pentane. polymer was dried in vacuo for 12 hours at room temperature to yield 2.66 g of fine powder (3010 turnovers/Ni). The polymer was mixed with 200 ml of MeOH in a blender at high speed to produce a fine 10 powder. The solid was collected by filtration and then mixed for 1 hour with 39 ml of a 1:1 mixture of MeOH/concentrated aqueous HCl. The solid was collected by filtration, washed with distilled water, and then washed on the filter 3X with 20 ml of a 2 wt. % 15 solution of Irganox® 1010 in acetone. The polymer was dried in vacuo for 12 hours at room temperature. DSC (25 to 300°C, 10°C/min, controlled cool at 10°C/min, second heat): Tg = 98°C, Tm(onset) = 160°C, Tm (end) = 240°C, Heat of fusion = 17 J/g. TGA(air, 10°C/min): 20 T(onset of loss) = 330°C. T(10% loss) = 450°C. ¹³C NMR (500 MHz 1H frequency, 3.1 ml of 1,2,4trichlorobenzene, 0.060g Cr(acac)3, 120°C): 30.640 (s, 2C), 38.364 (s, 1C), 46.528 (s, 2C). This spectrum is consistent with an addition polymer of cyclopentene 25 with cis-1,3-enchainment. A sample of the polymer was melted in a Schlenk tube under a nitrogen atmosphere. Fibers were drawn from the molten polymer using a stainless steel cannula with a bent tip. A nitrogen purge was maintained during the fiber drawing. 30 fibers were tough and could be drawn about 2X by pulling against a metal surface heated to 125°C.

Example 317

The complex [(2,4,6-MePh)₂DABAn]NiBr₂ was weighed into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) was added. A solution of EtAlCl₂ was added while stirring (0.73 ml, 1.0 M in hexanes, 50

equivalents/Ni). After stirring for 168 hours, the colution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 4.66 g of fine powder (4660 turnovers/Ni). polymer was mixed with 200 ml of MeOH in a blender at high speed to produce a fine powder. The solid was collected by filtration and then mixed for 1 hour with 39 ml of a 1:1 mixture of MeOH/concentrated aqueous The solid was collected by filtration, washed 10 with distilled water, and then washed on the filter 3X with 20 ml of a 2 wt. % solution of Irganox 1010 in acetone. The polymer was dried in vacuo for 12 hours at room temperature. DSC (25 to 350°C, 15°C/min, second heat): Tg = 97°C, Tm(onset) = 160°C, Tm (end) = 15 285°C, Heat of fusion = 25 J/g. 13 C NMR (500 MHz 1 H frequency, 3.1 ml of 1,2,4-trichlorobenzene, 0.060g Cr(acac)₃, 120°C): 30.604 (s, 2C), 38.333 (s, 1C), 46.492 (s, 2C). This spectrum is consistent with an addition polymer of cyclopentene with cis-1,3-20 enchainment. A sample of the polymer was melted in a Schlenk tube under a nitrogen atmosphere. Fibers were drawn from the molten polymer using a stainless steel cannula with a bent tip. A nitrogen purge was maintained during the fiber drawing. The fibers were 25 tough and could be drawn about 2X by pulling against a metal surface heated to 125 °C. GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run at 100°C in tetrachloroethylene, polystyrene calibration): Peak MW = 137,000; $M_n = 73,000$; $M_w = 298,000$; $M_w/M_n = 4.08$. 30

Example 318

The complex {[(2,6-i-PrPh)2DABMe2]PdMe(Et20)}+SbF6-(0.05 g, 0.060 mmol) was added to 10.0 g of stirring cyclopentene. Solid polymer formed rapidly and precipitated. The polymer was isolated by filtration, washed on the filter 3X with pentane, and dried in vacuo at room temperature to give 1.148 g finely divided powder (282 turnovers/Pd). DSC (25 to 350°C,

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15°C/min, first heat): Tm(onset) = 175°C, Tm (end) = 2^{5} °C, Heat of fusion = 16 J/g.

Example 319

The complex {[(2,6-i-

 $PrPh)_2DABMe_2]PdCH_2CH_2CH_2C(0)OCH_3\}+SbF_6^-$ (0.05 g, 0.059 mmol) was added to 10.0 g of stirring cyclopentene. The complex is not very soluble in cyclopentene. The amount of solids increased slowly. After 27 days, the solid polymer was isolated by filtration, washed on the filter 3X with pentane, and dried in vacuo at room 10 temperature to give 1.171 g finely divided powder (292 turnovers/Pd). DSC (25 to 350°C, 15°C/min, first heat): Tm(onset) = 170°C, Tm (end) = 255°C, Heat of fusion = 24 J/g.

Example 320

15 The complex [(2,6-i-PrPh)2DABMe2]NiBr2 was weighed into a glass vial in the dry box (0.025 g, 0.040 mmol). Cyclopentene (10.0 g, 1,000 equivalents/Ni) was added. A solution of MMAO was added while stirring (0.802 ml, 2.5 M in heptane, 50 equivalents/Ni). After stirring 20 for 5 minutes, the mixture was rusty brown and still contained some solids. An additional 50 equivalents of MMAO were added and the solution became homogeneous. After 12 hours, the mixture was filtered and the solids were washed several times on the filter with pentane. 25 The polymer was dried in vacuo for 12 hours at room temperature to yield 0.238 g of fine powder (87 turnovers/Ni). DSC (25 to 350°C, 15°C/min, second heat): Tm(onset) = 170°C, Tm (end) = 265°C, Heat of fusion = 18 J/g. 30

Example 321

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) and anhydrous methylene chloride (48.5 ml) were added. A solution of EtAlCl₂ was added while stirring (2.92 ml, 1.0 M in toluene, 200 equivalents/Ni). After stirring for 163 hours, the solution was filtered and

the solids were washed several times on the filter with pantane. The polymer was dried in vacuo for 12 hours at room temperature to yield 1.64 g of fine powder (1640 turnovers/Ni). A DSC thermal fractionation experiment was done according to the procedure of Example 312. A DSC was then recorded from 0°C to 330°C at 10°C/min. Tg = 92°C, Tm (onset) = 150°C, Tm (end) = 250°C, Heat of fusion = 11.4 J/g.

Example 322

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed 10 into a glass vial in the dry box (0.0093 g, 0.0146 mmol). Cyclopentene (10.0 g, 10,000 equivalents/Ni) was added. A solution of i-BuAlCl2 was added while stirring (2.92 ml, 1.0 M in toluene, 200 equivalents/Ni). After stirring for 163 hours, the 15 solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 1.99 g of fine powder (1990 turnovers/Ni). polymer was pressed at 292°C to give a transparent, 20 light gray, tough film. A DSC thermal fractionation experiment was done according to the procedure of Example 312. A DSC was then recorded from 0°C to 330°C at 10 °C/min. Tg = 103°C, Tm (onset) = 150°C, Tm (end) = 290°C, Heat of fusion = 27 J/g. 25

Example 323

The complex [(2,4,6-MePh)₂DABAn]NiBr₂ was weighed into a glass vial in the dry box (0.0932 g, 0.146 mmol). Cyclopentene (5.0 g, 500 equivalents/Ni) and toluene (6.54 ml) were added. A solution of PMAO (Akzo Nobel Polymethylaluminoxane) was added while stirring (3.16 ml, 2.32 M Al in toluene, 50 equivalents/Ni). After stirring for 163 hours, the solution was filtered and the solids were washed several times on the filter with pentane. The polymer was dried in vacuo for 12 hours at room temperature to yield 3.64 g of fine powder (364 turnovers/Ni). The polymer was pressed at 292°C to give a brown film that seemed tough, but

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failed along a straight line when it broke. A DSC thermal fractionation experiment was done according to the procedure of Example 312 was then recorded from 0°C to 330°C at 10°C/min. Tg = 100°C, Tm (onset) = 150°C, Tm (end) = 270°C, Heat of fusion = 21 J/g.

Example 324

A mixture of 20mg (0.032mmol) of NiBr2[(2,6-i-PrPh) 2DABMe2] was magnetically-stirred under nitrogen in a 50-mL Schlenk flask with 15mL of dry, deaerated toluene as 0.6mL of 3M poly(methylalumoxane) was 10 The mixture became deep blueinjected via syringe. black. Then 2.5mL (14mmol) of beta-citronellene, $(CH_3)_2C=CHCH_2CH_2CH(CH_3)CH=CH_2$, was injected and the mixture was immediately pressurized with ethylene at 190 kPa (absolute) and was stirred at 23°C for 17h; by 15 the end of 17h, the solution was too thick to stir. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was decanted. polymer was stirred with refluxing methanol for an hour to extract solvent; oven-drying yielded 0.90g of 20 rubbery polyethylene. ¹H NMR (CDCl₃) showed a CH₂:CH₃ ratio of 83:12, which is 101 CH3's per 1000 CH2's; there were small peaks for the beta-citronellene isopropylidene dimethyls (1.60 and 1.68ppm), as well as a tiny peak for vinyl H (5.0ppm); diene incorporation 25 was estimated at 0.7mol%. Differential scanning calorimetry: -51°C (Tg). GPC data (trichlorobenzene, 135°C; PE standard): Mn=23,200; Mw=79,200; Mz=154,000; Mw/Mn=3.42.

Example 325

A 15-mg (0.024-mmol) sample of NiBr2[(2,6-i-PrPh)2DABMe2] was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry, deaerated toluene and 5mL (27mmol) of dry, deaerated 1,9-decadiene. Then 0.6mL of polymethylalumoxane (1.7M MAO in heptane; contains about 30% isobutyl groups) was injected; the tan suspension did not change color. The mixture was pressurized with ethylene to 190 kPa

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(absolute) and was stirred for 1hr; it began to grow oreen-gray and darker in color, so 0.6mL more MAO was added, after which the mixture soon turned deep greenblack. The reaction was stirred for 16hr and the ethylene was then vented; by this time the solution had become thick and unstirrable. The mixture was stirred with refluxing 6N HCl and methanol, and the polymer was washed with methanol, pressed free of solvent, and dried under high vacuum to yield 1.0g of rubbery polyethylene. The polymer was insoluble in hot dichlorobenzene, demonstrating incorporation of the diene.

Example 326

A 21-mg (0.034-mmol) sample of NiBr₂[(2,6-i-PrPh) 2DABMe2] was magnetically stirred under nitrogen 15 in a 50-mL Schlenk flask with 25mL of dry, deaerated Then 0.6mL of 2.9M polymethylalumoxane was injected; the red-brown suspension became deep green. The mixture was purged with ethylene and then 2.0mL (1.4g; 15mmol) of 2-methyl-1,5-hexadiene was added; the 20 mixture was pressurized with ethylene to 190 kPa and was stirred for 18h; the solution became brown. ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was separated; rotary evaporation of the toluene layer yielded, after 25 acetone washing to remove catalyst, 47mg of viscous 1H NMR (CDCl3) showed a CH2:CH3 ratio liquid polymer. of 82:15, which is 130 CH3's per 1000 CH2's. There were also peaks for the incorporated diene at 1.72ppm (0.5H; $CH_3-C=CH_2$) and 4.68ppm (0.3H; $CH_3-C=CH_2$) and no 30 evidence of terminal vinyl (-CH=CH2; 4.95 and 5.80ppm) from unincorporated diene. The level of diene incorporation was about 0.7mol%. .

Example 327

A 30-mg (0.049-mmol) sample of NiBr2[(2,6-i-PrPh)2DABMe2] was magnetically stirred under nitrogen in a 50-mL Schlenk flask with 25mL of dry, deaerated toluene. Then 1.0mL of methylalumoxane (1.7M in

heptane; contains about 30% isobutyl groups) was 'njected; the red-brown suspension became deep green. The mixture was saturated with ethylene and then 0.5mL (0.38g; 3.0mmol) of 2-methyl-2,7-octadiene was added; the mixture was pressurized with ethylene to 190 kPa (absolute) and was stirred for 18h; the solution became brown. The ethylene was vented and the toluene solution was stirred with 6N HCl and methanol and was separated; rotary evaporation of the toluene yielded, after acetone washing to remove catalyst, 0.15g of viscous liquid polymer. ¹H NMR (CDCl₃) showed a CH₂:CH₃ ratio of 81.5:13.5, which is 117 CH₃'s per 1000 CH₂'s. The level of diene incorporation was about 0.5-1.0mol%, judging from the diene isopropylidene methyls

15 at 1.60 and 1.69ppm.

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Examples 328-335

C(R)=NAr)PdMe(OEt₂)]BAF with H₂C=CHC(O)OR' and on a preparative scale by the reaction of NaBAF with (ArN=C(R)-C(R)=NAr)PdMeCl and H₂C=CHC(O)OR' (vide infra). In these examples, the following labeling scheme is used to identify the different chelate complexes that were observed and/or isolated. Assignments of all ¹H NMR chelate resonances were confirmed by homonuclear decoupling experiments.

General Procedure for the Synthesis of Chelate Complexes

A gastight microliter syringe was used to add 1.1 equiv of H₂C=CHC(O)OR' to a mixture of 1 equiv of NaBAF and 1 equiv of [(2,6-i-PrPh)₂DABR₂)PdMeCl suspended in 25 mL of Et₂O. The sides of the Schlenk flask were rinsed with an additional 25 mL of Et₂O and the reaction mixture was stirred for 1-2 days at RT. Sodium chloride was removed from the reaction mixture via filtration, yielding a clear orange solution. The Et₂O was removed in vacuo and the product was washed with hexane and dried in vacuo. For R' = Me or t-Bu, no further purification was necessary (yields > 87%). Recrystallization lowered the yield of product and did not result in separation of the isomeric mixtures.

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For R' = $-CH_2(CF_2)_6CF_3$, contamination of the product with unreacted NaBAF was sometimes observed. Filtration of a CH_2Cl_2 solution of the product removed the NaBAF. The CH_2Cl_2 was then removed in vacuo to yield a partially oily product. A brittle foam was obtained by dissolving the product in Et_2O and removing the Et_2O in vacuo (yields > 59%). Although isolable, chelate complexes derived from FOA tended to be less stable than those derived from MA or t-BuA and decomposed with time or additional handling.

Spectral Data for the BAF Counterion The following $^1\mathrm{H}$ and $^{13}\mathrm{C}$ spectroscopic assignments of the BAF counterion in $\mathrm{CD}_2\mathrm{Cl}_2$ were invariant for different

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complexes and temperatures and are not repeated in the rectroscopic data for each of the cationic complexes: (BAF). 1 H NMR (CD₂Cl₂) δ 7.74 (s, 8, H_O), 7.57 (s, 4, H_D); 13 C NMR (CD₂Cl₂) δ 162.2 (q, JCB = 37.4, Cipso), 135.2 (C_O), 129.3 (q, JCF = 31.3, C_m), 125.0 (q, JCF = 272.5, CF₃), 117.9 (C_D).

Example 328

The above synthesis using [(2,6-i-PrPh)₂DABH₂]PdMeCl (937 mg, 1.76 mmol), NaBAF (1.56 g, 1.75 mmol), and MA (175 μL , 1.1 equiv) was followed and 10 the reaction mixture was stirred for 12 h. resulting orange powder (2.44 g, 96.0%) consisted of a mixture of 6a(Me) (91%), 5'a(Me) (5%), and 5a(Me) (4%), according to ¹H NMR spectroscopy. **6a(Me):** (CD₂Cl₂, 400 MHz, rt) δ 8.31 and 8.26 (s, 1 each, 15 N=C(H)-C'(H)=N), 7.5 - 7.2 (m, 6, Haryl), 3.17 (s, 3, OMe), 3.14 and 3.11 (septet, 2 each, CHMe2 and C'HMe2), 2.48 (t, 2, J = 5.8, $CH_2C(O)$), 1.75 (t, 2, J = 5.8, $PdCH_2$), 1.38, 1.32, 1.25 and 1.22 (d, 6 each, J = 6.8, CHMeMe' and C'HMeMe'), 0.73 (pentet, 2, J = 5.8, 20 PdCH₂CH₂C(0)); ¹³C NMR (CD₂Cl₂, 100 MHz, rt) 183.9 (C(O)), 167.1 ($J_{CH} = 181.4$, N=C(H)), 160.7 ($J_{CH} = 181.4$) 181.3, N=C'(H)), 142.9 and 142.4 (Ar, Ar': Cipso), 139.7 and 138.7 (Ar, Ar': Cipso), 129.8 and 129.0 (Ar, $Ar': C_p)$, 124.6 and 124.1 (Ar, $Ar': C_m$), 55.2 (OMe), 25 35.9 and 32.3 (PdCH₂CH₂CH₂C(O)), 29.3 and 29.1 (CHMe₂, $C'HMe_2$), 23.8 (PdCH₂CH₂CH₂C(O)), 24.5, 23.9, 23.2 and 22.5 (CHMeMe', C'HMeMe'); IR (CH₂Cl₂) 1640 cm⁻¹ [v(C(O))]. 5'(H,Me): ¹³C NMR (CD₂Cl₂, 100 MHz, rt) δ 193.2 (C(O)). Anal. Calcd for (C63H57BF24N2O2Pd): C, 30 52.28; H, 3.97; N, 1.94. Found: C, 52.08; H, 3.75; N, 1.61.

Example 329

The above synthesis using [(2,6-i- $PrPh)_2DABMe_2$] PdMeCl (634 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and MA (112 μ L, 1.1 equiv) was followed. The reaction mixture was stirred for 2 days and the product was recrystallized from CH₂Cl₂ at -30 °C to

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give 956 mg of orange crystals (57.3%, 2 crops). crystals consisted of a mixture of 6b(Me) (87%), 5'b (Me) (11.5%), and 5b (Me) (1.5%), according to ^{1}H NMR spectroscopy. 6b(Me): ^{1}H NMR (CD2Cl2, 400 MHz, rt) $^{\delta}$ 7.43 - 7.26 (m, 6, H_{aryl}), 3.03 (s, 3, OMe), 2.95(septet, 2, J = 6.79, $CHMe_2$), 2.93 (septet, 2, J =6.83, $C''HMe_2$), 2.39 (t, 2, J = 5.86, $CH_2C(O)$), 2.22 and 2.20 (N=C(Me)-C'(Me)=N), 1.41 (t, 2, J = 5.74, $PdCH_2$), 1.37, 1.30, 1.25 and 1.21 (s, 6 each, J = 6.80 10 - 6.94, CHMeMe', C'HMeMe'), 0.66 (pentet, 2, J = 5.76, $PdCH_2CH_2CH_2C(O)$); ¹³C NMR (CD₂Cl₂, 100 MHz, rt) δ 183.4 (C(O)), 178.7 and 171.6 (N=C-C'=N), 140.8 and 140.5 (Ar, Ar': Cipso), 138.6 and 138.0 (Ar, Ar': Co), 129.3 and 128.3 (Ar, Ar': Cp), 124.9 and 124.4 (Ar, Ar': C_m), 54.9 (OMe), 35.8 and 30.3 (PdCH₂CH₂CH₂C(O)), 15 29.5 and 29.2 (CHMe2, C'HMe2), 23.7 (PdCH2CH2CH2C(O)), 23.91, 23.86, 23.20 and 23.14 (CHMeMe', C'HMeMe'), 21.6 and 19.9 (N=C(Me)-C'(Me)=N); IR (CH_2Cl_2) 1643 cm⁻¹ [v(C(O))]. 5'b(Me): ¹H NMR (CD₂Cl₂, 400 MHz, rt) δ 3.47 (s, 3, OMe), 2.54 (m, 1, CHMeC(O)), 2.19 and 2.18 20 (s, 3 each, N=C(Me)-C'(Me)=N), 1.02 (d, 3, J=7.23, CHMeC(O)); 13 C NMR (CD₂Cl₂, 100 MHz, rt) δ 194.5 (C(O)), 179.2 and 172.2 (N=C-C'=N), 55.6 (OMe), 44.3 (CHMeC(O)), 28.4 $(PdCH_2)$, 21.2 and 19.6 (N=C(Me)-C)C'(Me) = N), 18.1 (CHMeC(O)). 5b(Me): ¹H NMR (CD₂Cl₂, 25 400 MHz, rt) δ 0.26 (d, 3, PdCHMe). Anal. Calcd for $(C_{65}H_{61}BF_{24}N_{2}O_{2}Pd): C, 52.92; H, 4.17; N, 1.90.$

Example 330

Found: C, 52.91; H, 4.09; N, 1.68.

The above synthesis was followed using [(2,6-i-PrPh)₂DABAn]PdMeCl (744 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and MA (112 μ L, 1.1 equiv). The reaction mixture was stirred for 2 days and the product was recrystallized from CH₂Cl₂ at -30°C to give 600 mg (33.8%, 2 crops) of a mixture of 6c(Me) (85%), 5'c(Me) (8%), 5''c(Me) (6%), and 5c(Me) (1%), according to ¹H NMR spectroscopy. 6c(Me): ¹H NMR (CD₂Cl₂) 400 MHz, rt) δ 8.17 (d, 1, J = 8.37, An: Hp), 8.15 (d, 1, J =

- 3.49, An': H'p), 7.62 7.40 (m, 8, An, An': H_m, H'm; * x: H_m, H_p; Ar': H'm, H'p), 7.08 (d, 1, J = 7.19, An: H_o), 6.60 (d, 1, J = 7.44, An': H'o), 3.37 (septet, 2, J = 6.79, CHMe₂), 3.33 (septet, 2, J = 6.86, C'HMe₂), 2.55 (t, 2, J = 5.93, CH₂C(O)), 1.79 (t, 2, J = 5.66, PdCH₂), 1.45, 1.42, 1.13 and 1.02 (d, 6 each, J = 6.79 6.90, CHMeMe', C'HMeMe'), 0.80 (pentet, 2, J = 5.82, PdCH₂CH₂CH₂C(O)); 13C NMR (CD₂Cl₂, 100 MHz, rt) δ 183.5 (C(O)), 175.3 and 168.7 (N=C-C'=N), 145.9 (An:
- 10 quaternary C), 141.3 and 140.5 (Ar, Ar': Cipso), 139.7 and 138.4 (Ar, Ar': C₀), 133.3 and 132.6 (An: CH), 131.9 (An: quaternary C), 129.8, 129.7, 129.6 and 128.5 (Ar, Ar': C_p; An: CH), 126.44 and 125.8 (An: quaternary C), 126.4 and 125.6 (An: CH), 125.5 and 124.6 (Ar, Ar':
- 15 C_m), 55.0 (OMe), 35.9 and 31.3 (PdCH₂CH₂CH₂C(O)), 29.7 and 29.4 (CHMe₂, C'HMe₂), 24.1 (PdCH₂CH₂CH₂C(O)), 24.1, 23.8, 23.32 and 23.27 (CHMeMe', C'HMeMe'); IR (CH₂Cl₂) 1644 cm⁻¹ [v(C(O))]. 5'c(Me): ¹H NMR (CD₂Cl₂, 400 MHz, rt) δ 3.64 (s, 3, OMe), 2.70 (m, 1, CHMeC(O)); ¹³C
- 20 NMR (CD₂Cl₂, 100 MHz, rt) δ 192.8 (C(O)). 5''c(Me): l_H NMR (CD₂Cl₂, 400 MHz, rt) δ 3.67 (s, 3, OMe), 2.46 (t, 2, J = 6.99, CH₂C(O)), 1.72 (t, 2, J = 7.04, PdCH₂). 5c(Me): l_H NMR (CD₂Cl₂, 400 MHz, rt) δ 0.44 (d, 3, PdCHMe).
- 25 Anal. Calcd for (C73H61BF24N2O2Pd): C, 55.80; H, 3.91; N, 1.78. Found: C, 55.76; H, 3.82; N, 1.62.

Example 331

The above synthesis was followed using [(2,6-i-PrPh)₂DABH₂]PdMeCl (509 mg, 0.954 mmol), NaBAF (845 mg, 0.953 mmol), and t-BuA (154 μL, 1.1 equiv). The reaction mixture was stirred for 1 day and yielded an orange powder (1.24 g, 87.3%) that was composed of a mixture of 6a(t-Bu) (50%), 5'a(t-Bu) (42%), and 5a(t-Bu) (8%), according to ¹H NMR spectroscopy. 6a(t-Bu): ¹H NMR (CD₂Cl₂, 400 MHz, rt) δ 8.27 and 8.25 (N=C(H)-C'(H)=N), 7.45 - 7.20 (m, 6, Haryl), 3.20 and 3.11 (septet, 2 each, J = 6.9, CHMe₂ and C'HMe₂), 2.42 (t, 2, J = 5.9, CH₂C(O)), 1.77 (t, 2, J = 5.3, PdCH₂),

1.39, 1.36, 1.22 and 1.21 (d, 6 each, J = 6.7, CHMeMe' and C'HMeMe'), 1.01 (s, 9, OCMe₃), 0.68 (pentet, 2, J =6.1, PdCH₂CH₂CH₂C(O)); ¹³C NMR (CD₂Cl₂, 100 MHz, rt, excluding Ar resonances) δ 182.6 (C(O)), 88.8 (OCMe₃), 37.8, 33.6 and 23.9 (PdCH₂CH₂C(O)), 29.3 and 29.0 (CHMe₂, C'HMe₂), 27.8 (OCMe₃), 24.8, 24.5, 22.7 and 22.6 (CHMeMe', C'HMeMe'); IR (CH2Cl2) 1615 cm⁻¹ $[v(C(O))]; 5'a(t-Bu): ^1H NMR (CD_2Cl_2, 400 MHz, rt;$ excluding Ar and i-Pr resonances) δ 8.29 and 8.22 (s, 1 each, N=C(H)-C'(H)=N, 2.53 (q, 1, J = 7.3, C(H) (Me) C(O)), 1.75 (d, 1, J = 8.9, PdCHH'), 1.53 (dd, 1, J = 9.0, 7.0, PdCHH'), 1.16 (OCMe₃); ¹³C NMR (CD₂Cl₂, 100 MHz, rt; excluding Ar resonances) δ 194.0 (C(O)), 90.6 $(OCMe_3)$, 45.9 (CHMeC(O)), 30.0 $(PdCH_2)$, 29.4, 29.3, 29.1 and 29.1 15

25 Example 332

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The above synthesis using [(2,6-i-PrPh)₂DABMe₂]PdMeCl (499 mg, 0.889 mmol), NaBAF (786 mg, 0.887 mmol), and t-BuA (145 μ L, 1.1 equiv) was followed. The reaction mixture was stirred for 1 day to yield an orange powder (1.24 g, 91.8%) that consisted of a mixture of 6b(t-Bu) (26%), 5'b(t-Bu) (63%), and 5b(t-Bu) (11%), according to ¹H NMR spectroscopy. ¹H NMR (CD₂Cl₂, 300 MHz, rt; diagnostic resonances only) 6b(t-Bu): δ 2.35 (t, 2, J = 6.1, CH₂C(O)), 0.97 (s, 9, 0CMe₃), 0.60 (pentet, 2, J = 5.7, PdCH₂CH₂CH₂C(O)); 5'b(t-Bu): δ 2.43 (q, 1, J = 7.2, CHMeC(O)), 1.08 (s, 9, 0CMe₃); 5b(t-Bu): δ 0.99 (s, 9, 0CMe₃), 0.29 (d, 3, J = 6.74, PdCHMe); ¹³C NMR (CD₂Cl₂,

75 MHz, rt; diagnostic resonances only) 6b(t-Bu): δ
182.3 (C(O)), 88.3 (OCMe3), 37.9 and 31.9
(PdCH₂CH₂CH₂C(O)), 27.9 (OCMe₃), 22.0 and 20.1
(N=C(Me)-C'(Me)=N); 5'b(t-Bu): δ 193.8 (C(O)), 178.8
5 and 171.8 (N=C-C'=N), 90.0 (OCMe₃), 45.8 (CHMeC(O)), 28.7 (PdCH₂), 21.1 and 19.6 (N=C(Me)-C'(Me)=N), 18.6 (CHMeC(O)); 5b(t-Bu) δ 190.7 (C(O)), 48.4 (CH₂C(O)), 33.9 (PdCHMe). Anal. Calcd for (C68H67BF₂4N₂O₂Pd): C, 53.82; H, 4.45; N, 1.85. Found: C, 53.62; H, 4.32; N, 1.55.

Example 333

The above synthesis was followed using [(2,6-i-Pr-Ph) 2DABAn] PdMeCl (503 mg, 0.765 mmol), NaBAF (687 mg, 0.765 mmol), and t-BuA (125 μ L, 1.1 equiv). reaction mixture was stirred for 1 day to yield an 15 orange powder (1.08 g, 87.8%) that consisted of a mixture of 6c(t-Bu) (47%), 5'c(t-Bu) (50%), and 5c(t-Bu)Bu) (3%), according to ¹H NMR spectroscopy. ¹H NMR (CD₂Cl₂, 300 MHz, rt; diagnostic chelate resonances only) 6c(t-Bu): δ 2.48 (t, 2, J = 6.05, $CH_2C(O)$), 1.80 20 $(t, 2, PdCH_2), 1.07 (s, 9, OCMe_3), 0.73 (pentet, 2, J =$ 5.87, $PdCH_2CH_2CH_2C(0)$); 5'c(t-Bu): δ 2.57 (q, 1, J = 6.96, CHMeC(O)), 1.58 (dd, 1, J = 8.80, 6.96, PdCHH'), 1.21 (s, 9, OCMe₃); 5c(t-Bu): δ 0.73 (d, 3, PdCHMe); 13C NMR (CD₂Cl₂, 75 MHz, rt; diagnostic chelate 25 resonances only) $6c(t-Bu): \delta 181.8 (C(0)), 87.9$ (OCMe₃), 37.4 and 32.2 (PdCH₂CH₂CH₂C(O)), 27.4 (OCMe₃); 5'c(t-Bu): δ 193.0 (C(O)), 89.5 (OCMe3), 45.5 (CHMeC(O)), 28.5 (PdCH₂), 27.2 (OCMe₃), 18.1 (CHMeC(O)). Anal. Calcd for (C76H67BF24N2O2Pd): 30 56.57; H, 4.19; N, 1.74. Found: C, 56.63; H, 4.06; N, 1.52.

Example 334

The above synthesis using [(2,6-i35 PrPh)₂DABH₂]PdMeCl (601 mg, 1.13 mmol), NaBAF (998 mg,
1.13 mmol), and FOA (337 μL, 1.1 equiv) yielded after 1
day of stirring 1.21 g (59.2%) of 6a(FOA) as a red
foam: ¹H NMR (CD₂Cl₂, 300 MHz, 0 ;C) δ 8.33 and 8.27
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(s, 1 each, N=C(H)-C'(H)=N), 7.4 - 7.2 (m, 6, Haryl), 3.85 (t, 2, JHF = 13.05, OCH₂(CF₂)₆CF₃), 3.13 and 3.08 (septet, 2 each, J = 6.9, CHMe₂ and C'HMe₂), 2.65 (t, 2, J = 5.62, CH₂C(O)), 1.74 (t, 2, J = 5.59, PdCH₂), 1.36, 1.29, 1.15 and 1.13 (d, 6 each, J = 6.73 - 6.82, CHMeMe', C'HMeMe'), 0.76 (pentet, 2, J = 5.44, PdCH₂CH₂CH₂C(O)).

Example 335

The above synthesis using [(2,6-i-

10 PrPh)₂DABMe₂] PdMeCl (637 mg, 1.13 mmol), NaBAF (1.00 g, 1.13 mmol), and FOA (339 μ L, 1.1 equiv) yielded after 1 day of stirring 1.36 g (65.2%) of **6b(FOA)** as a yellow foam: ¹H NMR (CD₂Cl₂, 300 MHz, 0 ;C) δ 7.5 - 7.0 (m, 6, Haryl), 3.64 (t, 2, JHF = 12.72, OCH₂(CF₂)6CF₃),

2.90 and 2.88 (septet, 2, J = 6.74, CHMe₂ and C'HMe₂),
2.56 (t, 2, J = 5.82, CH₂C(O)), 2.32 and 2.22 (N=C(Me) C'(Me)=N), 1.34, 1.27, 1.23 and 1.19 (d, 6 each, J =
6.75 - 6.82, CHMeMe', C'HMeMe'), 0.68 (pentet, 2, J =
5.83, PdCH₂CH₂CH₂C(O)).

Examples 336-338

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The labeling scheme given in Examples 328-335 is also used here. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Low-Temperature NMR Observation of Methyl Acrylate Olefin Complex Formation and Chelate Formation and 25 Rearrangement. One equivalent of MA was added to an NMR tube containing a 0.0198 M solution of $\{[(2,6$ $iPrPh)_2DABH_2]PdMe(OEt_2)]$ BAF in CD_2Cl_2 (700 μ L) at -78° C, and the tube was transferred to the precooled NMR After 14.25 min at -80°C, approximately 80% of 30 the ether adduct had been converted to the olefin complex. Two sets of bound olefin resonances were This observation is observed in a 86:14 ratio. consistent with the existence of two different rotamers of the olefin complex. Insertion of MA into the Pd-Me 35 bond occurred with predominantly 2,1 regiochemistry to give the 4-membered chelate 4a (Me) at -80;C ($t_{1/2} \sim 2.0$ The resonances for the major rotamer of the olefin

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complex disappeared before those of the minor rotamer. Much slower conversion of 4a(Me) to the 5-membered chelate 5a(Me) also began at -80°C. Upon warming to -60°C, complete and selective formation of 5a(Me) occurred in less than 4 h. The 5-membered chelate was relatively stable at temperatures below -50°C, however, upon warming to -20°C, rearrangement to the 6-membered chelate 6a(Me) was observed. NMR spectral data for the olefin complex, 4a(Me), and 5a(Me) follow. Spectral data for 6a(Me) is identical to that of the isolated chelate complex (see Examples 328-335).

Example 336

{[(2,6-i-PrPh)₂DABH₂] Pd (Me) [H₂C=CHC (O) OMe] }BAF.

1_H NMR (CD₂Cl₂, -80°C, 400 MHz) Major Rotamer: δ 8.45

15 and 8.32 (s, 1 each, N=C(H)-C'(H)=N), 7.5 - 7.1 (m, 6, Haryl), 5.14 (d, J = 15.2, HH'C=), 4.96 (dd, J = 14.9, 8.6, =CHC(O)), 4.63 (d, J = 8.5, HH'C=), 3.68 (s, 3, OMe), 3.03, 2.90, 2.80 and 2.67 (septet, 1 each, CHMe₂, C'HMe₂, C''HMe₂, C'''HMe₂), 1.5 - 1.0 (doublets, 24, CHMe₂), 0.61 (s, 3, PdMe); Minor Rotamer: δ 8.25 and 8.18 (s, 1 each, N=C(H)-C'(H)=N), 5.25 (d, 1, HH'C=), 4.78 (dd, 1, =CHC(O)), 4.58 (d, 1, HH'C=), 3.63 (OMe).

Example 337

Example 338

PdCHMe), 1.60 (d, 1, J = 18.6, CHH'C(0)), 1.34 (d, 6, J = 5.6, C'HMeMe' and C'''HMeMe'), 1.32 (d, 3, J = 6.2, CHMeMe'), 1.24 (d, 3, J = 6.8, C''HMeMe'), 1.18 (d, 6, J = 6.8, C'HMeMe' and C''HMeMe'), 1.15 (d, 3, J = 6.8, C'''HMeMe'), 1.08 (d, 3, CHMeMe'), 0.35 (d, 3, J = 6.9, PdCHMe); ¹³C NMR (CD₂Cl₂, 100 MHz, -80°C) δ 190.5 (C(O)), 166.1 $(J_{CH} = 181, N=C(H))$, 160.7 $(J_{CH} = 181, N=C(H))$ N=C'(H)), 142.8 and 141.6 (Ar, Ar': Cipso), 139.0, 138.6, 138.2 and 137.7 (Ar: Co, Co' and Ar': Co, Co'), 128.8 and 128.2 (Ar, Ar': Cp), 124.1, 123.54, 123.48, 10 123.4 (Ar: C_m , C_m ' and Ar': C_m , C_m '), 55.5 (OMe), 45.1 $(CH_2C(0))$, 35.6 (PdCHMe), 28.8, 28.5, 28.1 and 27.8 (CHMe₂, C'HMe₂, C''HMe₂, C'''HMe₂), 25.6, 24.2, 23.1, 23.0, 22.7, 22.3, 21.9, 21.3, and 21.3 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe' and PdCHMe). 15

Example 339-342

The labeling scheme given in Examples 328-335 is also used for Examples 339-342. Spectral data for the BAF counterion is the same as given in Examples 328-335.

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Low-Temperature NMR Observation of t-Butyl Acrylate Olefin Complex Formation and Chelate Formation and Rearrangement. One equiv of t-BuA was added to an NMR tube containing a 0.0323 M solution of $\{[(2,6-i PrPh)_2DABH_2]PdMe(OEt_2)$ BAF in CD_2Cl_2 (700 μ L) at -78°C, and the tube was transferred to the precooled NMR The olefin complex was observed at -80°C, and the probe was then warmed to -70°C. After 1 h at -70° C, conversion to 5a(t-Bu) and 5'a(t-Bu) was almost complete, with small amounts (<10%) of the olefin 30 complex and 4a(t-Bu) still present. Conversion of 5a(t-Bu) to 6a(t-Bu) was followed at -10°C $(t_{1/2}-1 h)$. When this experiment was repeated using 5 equiv of t-BuA, conversion to 5a, 5'a and 6a was observed at -80° After allowing the solution to stand at rt for 5 days, partial conversion to the unsubstituted 5membered chelate 5''a(t-Bu) was observed. Spectral data for the olefin complex, 4a(t-Bu), 5a(t-Bu) and

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5''a(t-Bu) follow. Spectral data for 5'a(t-Bu) and 6a(t-Bu) are identical to that of the isolated chelate complexes (see Examples 328-335).

Example 339

 $\left\{ \left[(2,6-i-PrPh)_2DABH_2 \right] PdMe \left[H_2C=CHC(O)O-t-Bu \right] \right\} BAF. \\ 1_{H} \ NMR \ \left(CD_2Cl_2, \ 400 \ MHz, \ -80;C \right) \ \delta \ 8.45 \ and \ 8.30 \ (s, \ 1) \\ each \ N=C(H)-C'(H)=N), \ 7.4 - 7.2 \ (m, \ 6, \ Haryl), \ 5.15 \ (d, \ 1, \ J=15.3, \ HH'C=), \ 4.89 \ (dd, \ 1, \ J=14.7, \ 8.4, \ =CHC(O)), \ 4.61 \ (d, \ 1, \ J=7.7, \ HH'C=), \ 2.92, \ 2.90, \ 2.80 \\ 10 \ and \ 2.64 \ (septets, \ leach, \ CHMe_2, \ C'HMe_2), \ C''HMe_2 \ and \ C'''HMe_2), \ 1.31 \ (s, \ 9, \ OCMe_3), \ 1.5 - 0.8 \ (doublets, \ 24, \ CHMe_2), \ 0.60 \ (s, \ 3, \ PdMe).$

Example 340

 $\left\{ \left[(2,6-i-PrPh)_2DABH_2 \right] Pd \left[CHEtC(0) 0-t-Bu \right] \right\} BAF \ 4a(t-1) Bu). \ \ \, ^{1}H \ NMR \ (CD_2Cl_2, \ 400 \ MHz, \ -70°C) \ \delta \ 8.22 \ and \ 8.21 \ (s, 1 each, N=C(H)-C'(H)=N), \ 2.21 \ (d, 1, J=9.2, PdCHEt), \ 0.71 \ (t, 3, J=7.9, PdCH(CH_2Me)), \ 0.5 \ and \ -0.4 \ (br m, 1 each, PdCH(CHH'Me)).$

Example 341

 $\left\{ \left[(2,6-i-PrPh)_2DABH_2 \right] Pd \left[CHMeCH_2C (0) O-t-Bu \right] \right\} BAF$ $5a(t-Bu). \quad 1H \ NMR \ \left(CD_2Cl_2, \ 400 \ MHz, \ -40^{\circ}C \right) \quad \delta \ 8.28 \ and$ $8.24 \ (s, \ 1 \ each, \ N=C(H)-C'(H)=N), \ 7.4 - 7.2 \ (m, \ 6, \ Haryl), \ 3.44, \ 3.32, \ 2.96 \ and \ 2.86 \ (septet, \ 1 \ each, \ CHMe_2, \ C''HMe_2, \ C'''HMe_2), \ 2.94 \ (dd, \ 1, \ J=18.6, \ 7.1, \ CHH'C(O)), \ 1.79 \ (pentet, \ 1, \ J=6.7, \ PdCHMe), \ 1.62 \ (d, \ 1, \ J=18.5, \ CHH'C(O)), \ 1.4 - 1.0$ $(doublets, \ 24, \ CHMe_2), \ 1.10 \ (s, \ 9, \ OCMe_3), \ 0.22 \ (d, \ 3, \ J=6.9, \ PdCHMe).$

Example 342

Example 343

The labeling scheme given in Examples 328-335 is also used for Example 343. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Low-Temperature NMR Observation of FOA Chelate
Formation and Rearrangement. One equiv of FOA was

added to an NMR tube containing a 0.0285 M solution of $\{[(2,6-i-PrPh)_2DABH_2]PdMe(OEt_2)\}BAF$ (1a) at -78;C in CD_2Cl_2 (700 μL), and the tube was briefly shaken at this temperature. A ¹H NMR spectrum at -80°C showed The sample was allowed to that FOA was not dissolved. warm slightly as it was shaken again and another spectrum was then acquired at -80°C. Approximately equal amounts of 5a(FOA) and 6a(FOA) were observed along with small amounts of the ether adduct la and FOA (an olefin complex was not observed). Rearrangement of 5a(FOA) to 6a(FOA) was observed at -40°C and was complete upon warming to -30°C. NMR spectral data for 5a(FOA) follow. Spectral data for 6a(FOA) are identical with that of the isolated complex (vide supra).

{[(2,6-i-

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Example 344

NMR Observation of {[(2,6-i-PrPh)₂DABH₂]Pd[CHR''CH₂CH₂C(O)OMe]}BAF and {[(2,6-i-PrPh)₂DABH₂]Pd[CH₂CH₂C(O)OMe]}BAF. A solution of {[(2,6-i-PrPh)₂DABH₂]PdMe(OEt₂)}BAF (21.5 mg, 0.0150 mmol) in 700 µL of CD₂Cl₂ was prepared at -78°C. Ethylene (5 equiv) was added via gastight syringe and the tube was shaken briefly to dissolve the ethylene. Methyl acrylate (5 equiv) was then added to the solution, also via gastight microliter syringe, and the tube was shaken briefly again. The tube was transferred to the NMR probe, which was precooled to -80°C. Resonances consistent with the formation of the ethylene adduct {[(2,6-i-PrPh)₂DABH₂]PdMe(H₂C=CH₂)}BAF

were observed. The solution was warmed and ethylene insertion was monitored at -40 to -20°C. consumption of one equiv of methyl acrylate occurred as the last equiv of ethylene disappeared, and resonances consistent with the formation of a substituted 6-5 membered chelate complex {[(2,6-i-PrPh) 2DABH2] Pd [CHR''CH2CH2C(O)OMe] BAF were observed [8.30 and 8.29 (N=C(H)-C'(H)=N), 3.17 (OMe)]. large upfield shift of the methoxy resonance is particularly diagnostic for formation of the 6-membered 10 chelate complex in these systems. The substituted 6membered chelate complex was observed at -20°C and initially upon warming to RT. After 2 h at RT, decomposition of the substituted 6-membered chelate complex had begun. After 24 h at RT, an additional 0.5 15 equiv of MA had been consumed and triplets at 2.42 and 1.66 ppm, consistent with the formation of the unsubstituted 5-membered chelate complex {[(2,6-i-PrPh) 2DABH2] Pd [CH2CH2C(O)OMe] BAF, were observed. Spectral data for the BAF counterion is the same as 20 given in Examples 328-335.

Example 345

NMR Observation of {[(2,6-i-PrPh) 2DABMe2] Pd (CHR' 'CH2CH2C(O)OMe] BAF. The procedure of Example 344 was followed with analogous results, 25 e.g., resonances for the formation of a substituted 6membered chelate complex {[(2,6-i-PrPh) 2DABMe2 Pd [CHR' 'CH2CH2C(O)OMe] BAF were observed following complete ethylene consumption [3.03 (s, OMe), 3.12, 2.96, 2.89, 2.83 (septets, CHMe2, C'HMe2, C'HMe2 30 and $C''' HMe_2$, 2.23 and 2.19 (s, N=C(Me)-C'(Me)=N)]. Again, the large upfield shift of the methoxy resonance is diagnostic for the formation of the six-membered chelate complex. The observation of four i-propyl methine resonances (vs. two i-propyl methine resonances 35 in the unsubstituted six-membered chelate complex) reflects the asymmetry introduced in the molecule due to the introduction of the R'' substituent on C_{α} of the

chelate ring and further supports the proposed structure. Spectral data for the BAF counterion is the same as given in Examples 328-335.

Example 346

5 {[(2,6-i-

PrPh) 2DABH2] Pd[CH2CH2CH2C(O)OMe] BAF. NMR data for the ethylene complex follow; it was observed in equilibrium with the starting chelate complex: $^1\text{H}\hat{\text{E}}\text{NMR}$ (CD2Cl2, 300 MHz, 182°K) δ 8.30 and 8.29 (s, 1 each, N=C(H)-

C'(H)=N), 7.38 - 7.24 (m, 6, H_{aryl}), 3.72 (s, 3, OMe),

- 3.43 (br s, 4, H₂C=CH₂), 3.10 (m, 2, CHMe₂), 2.70 (m,
 2, C''HMe₂), 2.20 (m, 2, CH₂C(O)), 1.25, 1.16, 1.09 and
 1.07 (d, 6 each, J = 7, CHMeMe', C'HMeMe'), 1.20 (PdCH₂
 (obscured by CHMeMe' peaks, observed by H,H-COSY)),
 0.56 (m, 2, PdCH₂CH₂CH₂C(O)); ¹³C NMR (CD₂Cl₂, 400 MHz,
- 20 -80°C) δ 178.9 (C(O)), 162.7 (J_{CH} = 179, N=C), 162.5 (J_{CH} = 179, N=C'), 141.3 and 140.5 (Ar, Ar': C_{ipso}), 138.5 and 138.1 (Ar, Ar': C_o), 128.5 and 128.3 (Ar, Ar': C_p), 124.1 and 124.0 (Ar, Ar': C_o), 122.9 (J_{CH} = 159.3, free H₂C=CH₂), 70.2 (J_{CH} = 158.6, bound
- 25 H₂C=CH₂), 53.0 (OMe), 36.5, 33.0 and 22.6 (PdCH₂CH₂CH₂C(O)), 27.8 (CHMe₂, C'HMe₂), 25.6, 25.3, 22.1 and 21.4 (CHMeMe', C'HMeMe'). Spectral data for the BAF counterion is the same as given in Examples 328-335.

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Example 347

{[(2,6-i-

PrPh)₂DABMe₂] Pd (H₂C=CH₂) [(CH₂CH₂CH₂C (O) OMe] }BAF. Ethylene was transferred at -78°C via gastight microliter syringe to an NMR tube containing a CD₂Cl₂ solution of the chelate complex { [(2,6-i-PrPh)₂DABMe₂] Pd [CH₂CH₂CH₂C (O) OMe] }BAF. NMR data for the ethylene complex follow; even at low temperature and in the presence of a large excess of ethylene, this

Example 348

{[(2,6-i-

 $PrPh)_2DABAn]Pd(H_2C=CH_2)[CH_2CH_2CH_2C(0)OMe]$ 15 Ethylene was transferred at -78°C via gastight microliter syringe to an NMR tube containing a CD_2Cl_2 solution of the chelate complex {[(2,6-i-PrPh) 2DABAn] Pd (CH2CH2CH2C(O)OMe)] BAF. NMR data for the ethylene complex follow; it was observed in equilibrium 20 with the starting chelate complex: ¹H NMR (CD₂Cl₂, 300 MHz, 178° K): δ 8.06 and 8.02 (d, J = 8, 1 each, An and An': H_p and H'_p), 7.50 - 7.38 (m, 8, An and An': H'_m and H_m , Ar: H_m and H_p), 6.48 (d, J = 7, 2, An and An': H_O and H'_O), 4.56 (br s, 4, $H_2C=CH_2$), 3.45 (s, 3, 25 OMe), 2.99 and 2.91 (m, 2 each, $CHMe_2$ and $C'HMe_2$), 1.77 $(m, 2, CH_2C(0)), 1.29, 1.27, 0.82$ and 0.77 (d, J = 6 -7, 6 each, CHMeMe', C'HMeMe') . H,H-COSY reveals that the remaining PdCH2CH2CH2C(O)-signals are obscured by the CHMe-signals at 1.2 ppm. Spectral data for the BAF 30 counterion is the same as given in Examples 328-335.

Example 349

{[(2,6-i-

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PrPh)₂DABH₂] Pd [CH₂CH₂CH₂C (O) OCH₂ (CF₂) 6CF₃] (H₂C=CH₂) BAF. Ethylene (0.78 equiv) was added via gastight microliter syringe to a 0.0105 M solution of the chelate complex {[(2,6-i-PrPh)₂DABH₂] Pd [CH₂CH₂C(O) OCH₂ (CF₂) 6CF₃] BAF in 333

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CD₂Cl₂ (700 μ L). NMR data for the ethylene complex follow; it was observed in equilibrium with the starting chelate complex: ¹H NMR (CD₂Cl₂, 300 MHz, 213.0°K) δ 8.40 and 8.25 (N=C(H)-C'(H)=N), 7.5 - 7.1 (m, 6, Haryl), 4.50 (t, 2, JHF = 13.39, OCH₂(CF₂)6CF₃), 4.41 (s, 4, H₂C=CH₂), 2.94 and 2.70 (septet, 2 each, CHMe₂, C'HMe₂), 1.80 (t, 3, CH₂C(O)), 1.4 - 1.0 (CHMeMe', C'HMeMe', PdCH₂CH₂CH₂C(O)). Spectral data for the BAF counterion is the same as given in Examples 328-335.

Example 350

A 12 mg (0.02 mmol) sample of [(2,6-i-PrPh) 2DABAn] NiBr2 was placed in a 25 mL high pressure The reactor was purged with argon. The reactor was cooled to 0°C before 2 mL of a 10 % MAO solution in toluene was added under a positive argon purge. reactor was filled (3/4 full) with liquid CO2 (4.5 MPa) and a 689 kPa head pressure of ethylene was added by continuous flow. A 6 degree exotherm was observed. A layer of polyethylene formed immediately at the ethylene CO2 interface. After 20 minutes, the cell was vented and the polyethylene removed from the reactor. The polymer was dried in vacuo for several hours. Polyethylene (2.05 g) was isolated; $M_n = 597,000, M_w/M_n$ = 2.29, T_{m} = 128°C. This example demonstrates the applicability of liquid CO2 as a solvent for polymerization in these catalyst systems.

Example 351

A 12 mg (0.02 mmol) sample of [(2,6-i-PrPh)2DABAn]NiBr2 was placed in a 25 mL high pressure cell and the reactor was purged with argon. The reactor was heated to 40°C and 2 mL of a 10 % MAO solution in toluene was added. CO2 (20.7 MPa) and ethylene (3.5 MPa, continuous flow) was then added to the reactor. Polyethylene began adhering to the sapphire window within minutes. After 20 minutes, the cell was vented and the polyethylene removed from the reactor. The polymer was dried in vacuo for several

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hours. Polyethylene (0.95 g) was isolated; $M_{\rm n}$ = 249,000, $M_{\rm w}/M_{\rm n}$ = 2.69, $T_{\rm m}$ = 113°C. This example demonstrates the applicability of supercritical CO₂ as a solvent for polymerization in these catalyst systems.

Example 352

A standard solution of [(2,6-i-PrPh)₂DABAn]NiBr₂ was prepared as follows: 1,2-difluorobenzene (10 mL) was added to 6.0 mg of [(2,6-i-PrPh)₂ DABAn]NiBr₂ (8.4 x 10⁻⁶ mol) in a 10 mL volumetric flask. The standard solution was transferred to a Kontes flask and stored under an argon atmosphere.

A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of [(2,6-i-PrPh)2DABAn]NiBr2 (8.3x10-7 mol), and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from 25°C to 45°C within seconds. Activation of the internal cooling system returned the reactor temperature to 30°C. After 10 minutes, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.0 g (1.8x106 TO/h) of polyethylene. Differential scanning calorimetry: $T_m = 118$ °C (133 J/g). Gel permeation

chromatography (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_{\rm n}=470,000$; $M_{\rm w}=1,008,000$; $M_{\rm w}/M_{\rm n}=2.14$. $^{13}{\rm C-NMR}$ analysis: total methyls/1000 CH₂ (27.6), methyl (21.7), ethyl (2.6), propyl (.7), butyl (1), amyl (.4).

Example 353

A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of [(2,6-i-PrPh)2DABAn]NiBr2 (8.3x10⁻⁷ mol), 335

and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.8 MPa as the internal temperature increased from 25°C to 48°C within seconds. Activation of the internal cooling system returned the reactor temperature to ~30°C. After 10 minutes, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H₂O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 8.85 g (2.3x106 TO/h) of polyethylene. DSC: $T_m = 122$ °C. (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n = 485,000; M_w = 1,042,000;$ $M_W/M_D = 2.15$. ¹³C-NMR analysis: total methyls/1000 CH₂ (21.3), methyl (16.3), ethyl (2.1), propyl (0.7), butyl (0.9), amyl (0.2).

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Example 354

A 1000 mL Parr® stirred autoclave under an argon atmosphere, was charged with 1 mL of a standard solution of $[(2,6-i-PrPh)_2DABAn]NiBr_2 (8.3x10^{-7} mol)$, and 200 mL of dry, deaerated toluene. The reactor was purged with ethylene before addition of 2 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 4.1 MPa as the internal temperature increased from 25°C to 45°C within seconds. Activation of the internal cooling system returned the reactor temperature to ~30°C. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.45 g (1.9x106 TO/h) of polyethylene. DSC: $T_m = 126$ °C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal

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calibration theory): $M_{\rm n}$ = 510,000; $M_{\rm w}$ = 1,109,000; $M_{\rm w}/M_{\rm n}$ = 2.17. ¹³C-NMR analysis: total methyls/1000 CH₂ (5.1), methyl (5.1), ethyl (0), propyl (0), butyl (0), amyl (0).

Example 355

A 1 mg (1.7x10⁻⁶ mol) sample of [(2,6-i-PrPh) 2DABH2] NiBr2 was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. reactor was purged with ethylene before addition of 1.5 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from 25°C to 45°C within seconds. Activation of the internal cooling system returned the reactor temperature to ~30°C. After 10 ' min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 14.1 g $(1.8 \times 10^6 \text{ TO/h})$ of polyethylene. DSC: $T_m = 126$ °C (151 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_n = 32,000$; $M_w =$ 89,000; $M_W/M_D = 2.75$.

Example 356

A 1 mg (1.7x10⁻⁶ mol) sample of [(2,6-i-PrPh)2DABH2]NiBr2 was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 1.5 mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.1 MPa as the internal temperature increased from 25°C to 50°C within seconds. Activation of the internal cooling system returned the reactor temperature to ~30°C. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was

recovered from the reactor collected and washed with 8 M HCl, H₂O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 16.1 g (2×10^6 TO/h) of polyethylene. DSC: T_m = 129°C (175 J/g). GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): M_n = 40,000; M_w = 89,000; M_w/M_n = 2.22.

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Example 357

A 1.2 mg (1.9x10⁻⁶ mol) sample of [(2,6-i-10 PrPh) 2DABMe2] NiBr2 was placed in a Parr® 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. reactor was purged with ethylene before addition of 2.0 mL of a 10% MAO solution in toluene. The autoclave was 15 rapidly pressurized with ethylene to 1.4 MPa as the internal temperature increased from 24°C to 31°C within seconds. Activation of the internal cooling system returned the reactor temperature to ~25°C. After 12 min, the ethylene was vented and acetone and water were 20 added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H₂O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 8 g (9x105 TO/h) of polyethylene. DSC: Broad melt beginning 25 approximately 0°C with a maximum at 81°C (25 J/g). GPC (trichlorobenzene, 135 °C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_{\rm H} = 468,000; M_{\rm W} = 1,300,000;$ $M_W/M_D = 2.81$. ¹³C-NMR analysis: total methyls/1000 30 CH₂ (46.6), methyl (37.0), ethyl (2.4), propyl (1.6), butyl (1.3), amyl (1.4).

Example 358

A 1.2 mg (1.9x10⁻⁶ mol) sample of [(2,6-i-35 PrPh)₂DABMe₂]NiBr₂ was placed in a Parr[®] 1000 mL stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. The reactor was purged with ethylene before addition of 2.0

mL of a 10% MAO solution in toluene. The autoclave was rapidly pressurized with ethylene to 2.8 MPa as the internal temperature increased from 24°C to 34°C within seconds. After 12 min, the ethylene was vented and acetone and water were added to quench the reaction. 5 Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 6.5 g (6x10⁵ TO/h) of polyethylene. Broad melt beginning approximately 60°C with a 10 maximum at 109°C (80 J/g). GPC (trichlorobenzene, 135° C, polystyrene reference, results calculated as polyethylene using universal calibration theory): 616,000; $M_W = 1,500,000$; $M_W/M_D = 2.52$. ¹³C-NMR analysis: total methyls/1000 CH₂ (32.0), methyl 15 (24.6), ethyl (2.6), propyl (1.3), butyl (0.6), amyl (1.3).

Example 359

A 1.2 mg $(1.9 \times 10^{-6} \text{ mol})$ sample of [(2,6-i-PrPh) 2DABMe2] NiBr2 was placed in a Parr® 1000 mL 20 stirred autoclave under argon. The autoclave was sealed and 200 mL of dry toluene was added. reactor was purged with ethylene before addition of 2.0 The autoclave was mL of a 10% MAO solution in toluene. rapidly pressurized with ethylene to 4.1 MPa. 25 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 7.2 g (7x105 30 TO/h) of polyethylene. GPC (trichlorobenzene, 135;C, polystyrene reference, results calculated as polyethylene using universal calibration theory): 800,000; $M_W = 1,900,000$; $M_W/M_D = 2.43$. $^{13}C-NMR$ analysis: total methyls/1000 CH2 (18.7), methyl 35 (14.9), ethyl (1.7), propyl (1.1), butyl (0.3), amyl (0.4).

Example 360

A 1.5 mg $(2.4 \times 10^{-6} \text{ mol})$ sample of [(2,6-i-PrPh) 2DABMe2] NiBr2 and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 50°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 6.25 g (6x10⁵ TO/h) of polyethylene. DSC: Broad melt beginning approximately -25°C with a maximum at 50°C; Tg = -36°C. GPC (trichlorobenzene, 135;C, polystyrene 15 reference, results calculated as polyethylene using universal calibration theory): $M_n = 260,000; M_w =$ 736,000; $M_W/M_{\Omega} = 2.83$.

Example 361

A 1.5 mg $(2.4 \times 10^{-6} \text{ mol})$ sample of [(2,6-i-20 PrPh) 2DABMe2] NiBr2 and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 65°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly 25 pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was 30 dried under high vacuum overnight to yield 7.6 g (7x105 TO/h) of polyethylene. DSC: Broad melt beginning approximately -50°C with a maximum at 24°C. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal 35 calibration theory): $M_n = 176,000$; $M_w = 438,000$; M_w/M_n = 2.49.

Example 362

A 1.5 mg $(2.4 \times 10^{-6} \text{ mol})$ sample of [(2,6-i-PrPh) 2DABMe2] NiBr2 and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 80°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly pressurized with ethylene to 690 kPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 10 M HCl, H_2O , and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.0 g (0.9x10⁵ TO/h) of polyethylene. DSC: Broad melt beginning approximately -50°C with a maximum at -12°C. GPC (trichlorobenzene, 15

GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_{\rm n}$ = 153,000; $M_{\rm w}$ = 273,000; $M_{\rm w}/M_{\rm n}$ = 1.79.

Example 363

A 1.5 mg $(2.4 \times 10^{-6} \text{ mol})$ sample of [(2,6-i-20 PrPh) 2DABMe2]NiBr2 and 200 mL of dry toluene was added to a Parr® 1000 mL stirred autoclave under an argon atmosphere. The reactor was heated to 80°C and purged with ethylene before addition of 3.0 mL of a 7% MMAO solution in heptane. The autoclave was rapidly 25 pressurized with ethylene to 2.1 MPa. After 10 min, the ethylene was vented and acetone and water were added to quench the reaction. Solid polyethylene was recovered from the reactor collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was 30 dried under high vacuum overnight to yield 1.05 g (0.9x10⁵ TO/h) of polyethylene. DSC: Broad melt beginning approximately -25°C with a maximum at 36°C.

Example 364

A standard solution of [(2,6-i-PrPh)2DABAn]NiBr2 was prepared as follows: 1,2-difluorobenzene (10 mL) was added to 6.0 mg of [(2,6-i-PrPh)2DABAn]NiBr2 (8.4x10⁻⁶ mol) in a 10 mL volumetric flask. The

standard solution was transferred to a Kontes flask and stored under an argon atmosphere.

A 250 mL Schlenk flask was charged with 1 mL of a standard solution of [(2,6-i-PrPh)2DABAn]NiBr2 (8.3x10-7 mol), and 100 mL of dry, deaerated toluene. flask was cooled to -20°C in a dry ice isopropanol bath and filled with ethylene (100 kPa, absolute) before addition of 1.5 mL of a 10% MAO solution in toluene. After 30 min, acetone and water were added to quench the reaction. Solid polyethylene was recovered from 10 the flask collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 0.8 g (7x104 TO/h) of polyethylene. GPC (trichlorobenzene, 135°C, polystyrene reference, results calculated as 15 polyethylene using universal calibration theory): $M_n =$ $519,000; M_W = 768,000; M_W/M_n = 1.48.$

Example 365

A 250 mL Schlenk flask was charged with 20 mg of

[(2,6-i-PrPh)2DABMe2]NiBr2 (3.2x10⁻⁵ mol), and 75 mL of
dry, deaerated toluene. The flask was cooled to 0°C
filled with propylene (100 kPa absolute) before
addition of 1.5 mL of a 10% MAO solution in toluene.
After 30 min, acetone and water were added to quench
the reaction. Solid polypropylene was recovered from
the flask and washed with 6 M HCl, H2O, and acetone.
The resulting polymer was dried under high vacuum
overnight to yield 0.15 g polypropylene. DSC: Tg = -31
°C. GPC (trichlorobenzene, 135°C, polystyrene

reference): Mn = 25,000; Mw = 37,000; Mw/Mn = 1.47.

Example 366

Cyclopentene (16 μ L, 10 eq) was added to a suspension of [(2,6-i-PrPh)₂DABAn]NiBr₂ (12 mg, 1.6x10⁻⁵ mol) in 50 mL of dry toluene. A 10% MAO solution (1.5 mL) in toluene was added and the homogenous mixture stirred for 2 h at 25°C. After 2 h, the flask was filled with ethylene (100 kPa, absolute) and the reaction stirred for 15 min. Acetone and water were

added to quench the polymerization and precipitate the Solid polyethylene was recovered from the flask collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 3.6 g (32,000 TO/h) 5 GPC: (trichlorobenzene, 135°C, polyethylene. polystyrene reference, results calculated as polyethylene using universal calibration theory): $M_{\rm n}$ = 87,000; $M_W = 189,000$; $M_W/M_D = 2.16$. A control experiment was run under identical conditions to that 10 described above except no cyclopentene was added to stabilize the activated nickel complex. Polyethylene (380 mg, 3500 TO/h) was isolated. This example demonstrates the applicability of the Ni agostic cation as a potential soluble stable initiator for the 15 polymerization of ethylene and other olefin monomers.

Example 367

1-Hexene (3 mL, 6 vol %) was added to a suspension of $[(2,6-i-PrPh)_2DABAn]NiBr_2$ (12 mg, 1.6x10⁻⁵ mol) in 50 mL of dry toluene. The flask was cooled to -20°C in 20 a dry ice isopropanol bath and 1.5 mL of a 10% MAO solution in toluene was added. After stirring the reaction for 1.5 h, acetone and water were added to quench the polymerization and precipitate the polymer. Solid poly(1-hexene) was recovered from the flask 25 collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 200 mg poly(1-hexene). (trichlorobenzene, 135°C, polystyrene reference): 44,000; $M_W = 48,000$; $M_W/M_{11} = 1.09$. 30

Example 368

1-Hexene (2.5 mL, 6 vol %) was added to a suspension of [(2,6-i-PrPh)2DABAn]NiBr2 (6 mg, 8.3x10⁻⁶ mol) in 50 mL of dry toluene. The flask was cooled to -10°C in a dry ice isopropanol bath and 1.5 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 1 h, acetone and water were added to quench the polymerization and precipitate the polymer.

Solid poly(1-hexene) was recovered from the flask and washed with 6 M HCl, H₂O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 250 mg poly(1-hexene). GPC (dichloromethane,

polystyrene reference): $M_{\rm n}$ = 51,000; $M_{\rm w}$ = 54,000; $M_{\rm w}/M_{\rm n}$ = 1.06.

Example 369

Propylene (1 atm) was added to a Schlenk flask charged with a suspension of [(2,6-i-PrPh)2DABAn]NiBr2 (12 mg, 1.7×10^{-5} mol) in 50 mL of dry toluene after 10 cooling the mixture to -15°C in a dry ice isopropanol bath. A 7% MMAO solution in heptane was added. After stirring the reaction for 30 min, acetone and water were added to quench the polymerization and precipitate the polymer. Solid polypropylene was recovered from 15 the flask and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 800 mg polypropylene. (dichloromethane, polystyrene reference): $M_n = 84,000$; $M_W = 96,000; M_W/M_D = 1.14$ 20

Example 370

Propylene (100 kPa, absolute) was added to a Schlenk flask charged with a suspension of [(2,6-i- $PrPh)_2DABAn]NiBr_2$ (12 mg, 1.7x10⁻⁵ mol) in 50 mL of dry toluene. After cooling the mixture to -15;C in a dry 25 ice isopropanol bath, a 7% MMAO solution in heptane was added. After stirring the reaction for 30 min, 5 mL of dry 1-hexene was added and the propylene removed in vacuo. The polymerization was allowed to stir for an additional 30 min before acetone and water were added 30 to quench the polymerization and precipitate the Solid polypropylene-b-poly(1-hexene) was recovered from the flask and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 1.8 g polypropylene-b-35 poly(1-hexene). GPC (dichloromethane, polystyrene reference): $M_n = 142,000$; $M_w = 165,000$; $M_w/M_n = 1.16$. 1H-NMR analysis: indicates the presence of both a

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polypropylene and poly(1-hexene) block. IH-NMR also suggests that the DP of the propylene block is substantially higher than the DP of the 1-hexene block. DSC analysis: $T_g = -18$ °C corresponding to the polypropylene block. No other transitions were observed.

Example 371

1-Octadecene (4 mL, 8 vol %) was added to a suspension of [(2,6-i-PrPh)2DABAn]NiBr2 (12 mg, 1.6x10- 5 mol) in 50 mL of dry toluene. The flask was cooled to -10°C in a dry ice isopropanol bath and 2 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 1 h, acetone and water were added to quench the polymerization and precipitate the polymer. Solid poly(1-octadecene) was recovered from the flask collected and washed with 6 M HCl, H2O, and acetone. The resulting polymer was dried under high vacuum overnight to yield 200 mg poly(1-octadecene). GPC (trichlorobenzene, 135°C, polystyrene reference): Mn = 19,300; $M_W = 22,700$; $M_W/M_{\Pi} = 1.16$. DSC: $T_m = 37$ °C. 20 1H-NMR (CDCl3) analysis 47 branches/1000 C (theoretical 56 branches/1000 C).

Example 372

A 12-mg (.022 mmol) sample of [(para-Me-Ph) 2DABMe2] NiBr2 was placed; in a Parr® 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene (reactor temperature was 65°C). The reactor was purged with ethylene and 1.5 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 min. A 15°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 20 g of ethylene oligomers. NMR (CDCl₃) analysis 83% α -olefin.

Example 373

A 12-mg (.022 mmol) sample of [Ph2DABAn] NiBr2 was placed in a Parr® 1000 mL stirred autoclave under an 345

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argon atmosphere with 200 mL of dry toluene (reactor temperature was 55°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 minutes. A 18°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 26 g (corrected for loss of C4, C6, and C8 during work-up) of ethylene oligomers. ¹H-NMR (CDCl₃) and GC analysis: Distribution: C4-C₁₈, C4 = 6.0%, C6 = 21%, C8 = 22%, C₁₀ = 17%, C₁₂ = 16%, C₁₄ = 13%, C₁₆ = 5%, C₁₈ = trace; 90% α-olefin.

Example 374

A 12-mg (.022 mmol) sample of [Ph2DABAn]NiBr2 was 15 placed in a Parr® 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene (reactor temperature was 45°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was 20 rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 min. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 32 g (corrected for loss of C4, C6, and C8 during work-up) of ethylene 25 oligomers. 1H-NMR (CDCl3) and GC analysis: Distribution: C_4-C_{20} , $C_4 = 9.0$ %, $C_6 = 19$ %, $C_8 = 19$ %, $C_{10} = 15\%$, $C_{12} = 14\%$, $C_{14} = 11\%$, $C_{16} = 5\%$, $C_{18} = 4\%$, $C_{20} = 2$ %; 92% α -olefin.

Example 375

A 12-mg (.022 mmol) sample of [(Ph)DABAn]NiBr $_2$ was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 2.1 MPa and the reaction was stirred for 30 min. A 20°C exotherm was observed. The

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oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 16.1g of a fluid/waxy mixture (50,000 To/h based on isolated oligomer). $^1\text{H-NMR}$ (CDCl₃) analysis 80% α -olefin. Distribution of isolated oligomers by GC analysis: $C_{10} = 20\%$, $C_{12} = 28\%$, $C_{14} = 23\%$, $C_{16} = 15\%$, $C_{18} = 10\%$, $C_{20} = 4\%$. All C_4 , C_6 , C_8 and some C_{10} was lost during work-up.

Example 376

A 12-mg (.022 mmol) sample of [(Ph)DABAn]NiBr2 was 10 placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was 15 rapidly pressurized to 4.1 MPa and the reaction was stirred for 60 minutes. A 20°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 28.3g of crude product (50,000 TO/h based 20 on isolated oligomer). Trace Al was removed by an aqueous/organic work-up of the crude mixture. 1H-NMR (CDCl₃) analysis 85% α -olefin. Distribution of isolated oligomers by GC analysis: $C_{10} = 13\%$, $C_{12} =$ 30%, $C_{14} = 26$ %, $C_{16} = 18$ %, $C_{18} = 10$ %, $C_{20} = 3$ %. All C_4 , 25 C_6 , C_8 and some C_{10} was lost during work -up.

Example 377

A 12-mg (.022 mmol) sample of [(Ph)DABAn]NiBr₂ was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of deaerated toluene (reactor temperature was 25°C). The reactor was purged with ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 6.7 MPa and the reaction was stirred for 60 min. A 15°C exotherm was observed. The oligomerization was quenched upon addition of acetone and water. The solvent was removed in vacuo resulting in 21.6g of crude product (40,000 TO/h based on

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isolated oligomer). 1H -NMR (CDCl $_3$) analysis 93% α -olefin. Distribution of isolated oligomers by GC analysis: C_{10} = 13%, C_{12} = 27%, C_{14} = 26%, C_{16} = 18%, C_{18} = 12%, C_{20} = 5%. All C_4 , C_6 , C_8 and some C_{10} was lost during work-up.

Example 378

A 12-mg (.022 mmol) sample of [Ph2DABAn] NiBr2 was placed in a 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene (reactor temperature was 50°C). The reactor was purged with 10 ethylene and 2 mL (100 eq) of a 10% MAO solution in toluene was added to the suspension. The autoclave was rapidly pressurized to 5.5 MPa and the reaction was stirred for 60 minutes. A 15°C exotherm was observed. The oligomerization was quenched upon addition of 15 acetone and water. The solvent was removed in vacuo resulting in 22.3g of crude product (40,000 TO/h based on isolated oligomer). 1H -NMR (CDCl $_3$) analysis 92% α olefin. Distribution of isolated oligomers by GC analysis: $C_{10} = 10\%$, $C_{12} = 28\%$, $C_{14} = 25\%$, $C_{16} = 19\%$, 20 $C_{18} = 12\%$, $C_{20} = 6\%$. All C_4 , C_6 , C_8 and some C_{10} was lost during work-up.

Examples 379-393

General Procedure for Copolymerizations

(a) Experiments at Ambient Pressure: A Schlenk 25 flask containing the catalyst precursor was cooled to -78°C, evacuated, and placed under an ethylene atmosphere. In subsequent additions, methylene chloride and the acrylate were added to the cold flask via syringe. The solution was allowed to warm to room 30 temperature and stirred with a magnetic stir bar. After the specified reaction time, the reaction mixture was added to ~600 mL of methanol in order to precipitate the polymer. Next, the methanol was decanted off of the polymer, which was then dissolved 35 in ~600 mL of Et20 or petroleum ether. copolymerizations with FOA, a second precipitation of the polymer solution into methanol was often necessary

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in order to remove all of the acrylate from the polymer.) The solution was filtered though a plug of Celite® and/or neutral alumina, the solvent was removed, and the polymer was dried in vacuo for several days. The copolymers were isolated as clear, free-flowing or viscous oils. The copolymers were often darkened by traces of palladium black, which proved difficult to remove in some cases. Polymers with high FOA incorporation were white, presumably due to phase separation of the fluorinated and hydrocarbon segments.

(b) Experiments at Elevated Pressure: Reactions were carried out in a mechanically stirred 300 mL Parr ® reactor, equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. A solution of 0.1 mmol of catalyst precursor in methylene chloride, containing the functionalized comonomer (5-50 mL, total volume of the liquid phase: 100 mL), was transferred via cannula to the reactor under a nitrogen atmosphere. After repeatedly flushing with ethylene or propylene, constant pressure was applied by continuously feeding the gaseous olefin and the contents of the reactor were vigorously stirred. After the specified reaction time, the gas was vented. Volatiles were removed from the reaction mixture in vacuo, and the polymer was dried under vacuum overnight. In representative runs, the volatile fraction was analyzed by GC for low-molecular-weight products. Residual monomers (tBuA, FOA) or homooligomers of the functionalized comonomer (MVK) were removed by precipitating the polymer from methylene chloride solution with methanol. This procedure did not significantly alter the polymer composition.

Copolymer Spectral Data. In addition to the signals of the methyl, methylene and methine groups originating from ethylene or propylene, the ¹H and ¹³C NMR spectra of the copolymers exhibit characteristic resonances due to the functionalized comonomer. The

IR-spectra display the carbonyl band of the functional groups originating from the comonomer.

Ethylene-MA Copolymer: ¹H NMR (CDCl₃, 400 MHz) δ 3.64 (s, OCH₃), 2.28 (t, J = 7, CH₂C(O)), 1.58 (m, CH₂CH₂C(O)); ¹³C NMR (C₆D₆, 100 MHz) δ 176 (C(O)), 50.9

 (OCH_3) ; IR (film): 1744 cm⁻¹ [v(C(O))].

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Ethylene-FOA Copolymer: ¹H NMR (CDCl₃, 400 MHz) δ 4.58 (t, J_{HF} = 14, OCH₂(CF₂)₆CF₃), 2.40 (t, J = 7, CH₂C(O)), 1.64 (m, CH₂CH₂C(O)); ¹³C NMR (CDCl₃, 100 MHz) δ 172.1 (C(O)), 59.3 (t, J_{CF} = 27, OCH₂(CF₂)₆CF₃);

10 MHz) δ 172.1 (C(O)), 59.3 (t, J_{CF} = 27, O,CH₂(CF₂)₆CF₃); IR (film): 1767 cm⁻¹ [v(C(O))].

Ethylene-tBuA Copolymer: ¹H NMR (CDCl₃, 300 MHz) δ 2.18 (t, J = 7, CH₂C(O)), 1.55 (m, CH₂CH₂C(O)), 1.42 (s, OCMe₃); ¹³C NMR (CDCl₃, 62 MHz) δ 173.4 (C(O)); IR (film): 1734 cm⁻¹ (CO).

Ethylene-MVK Copolymer: ¹H NMR (CDCl₃, 250 MHz) δ 2.39 (t, J = 7, CH₂C(O)), 2.11 (s, C(O)CH₃), 1.5 (m, CH₂CH₂C(O)); ¹³C NMR (CDCl₃, 62 MHz) δ 209 (C(O)); IR (film): 1722 cm⁻¹ [v(C(O))].

20 Propylene-MA Copolymer: ¹H NMR (CDCl₃, 250 MHz) δ 3.64 (s, OCH₃), 2.3 (m, CH₂C(O)); ¹³C NMR (CDCl₃, 62 MHz) δ 174.5 (C(O)), 51.4 (OCH₃); IR (film): 1747 cm⁻¹ [v(C(O))].

Propylene-FOA Copolymer: 1 H NMR (CDCl₃, 250 MHz) 25 δ 4.57 (t, JHF = 14, OCH₂(CF₂)₆CF₃), 2.39 (m, CH₂C(O)); 13_C NMR (CDCl₃, 62 MHz) δ 172.2 (C(O)), 59.3 (t, JCF = 27, OCH₂(CF₂)₆CF₃); IR (film): 1767 cm⁻¹ [v(C(O))].

Results of the various polymerization are given in the Table below.

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		попс	monomers	conc.		mass	comon	TONe	de l	M _n f	•
	Cart.		1	comon.	ptacm)	ролушет	Incorp. d	E re. P	Comon.	(x 10 3)	E/E
379	q ₉	ω	A	0.6 M	73	22.2	1.0	7710	78	88	1.8
380	Q9	Ö	Æ.	2.9 M	73	4.3	6.18	1296	84	56	1.6
381	q9	ы	AM /	5.8 M	7	1.8	12.1\$	455	63	Ħ	1.6
382	q ₉	ы	Æ.	5.8 ₹	9	11.2	4.0%	3560	148	. 42	1.8
383	6a	Ė	MA /	5.8 M	φ	1.2	5.0\$	355	19	0.39	1
384	Q 9	ы	₩ ₩	5.8 M	9	1.2	4.78	364	18	10	1.8
385	ą	E/	t BuA	3.4 M	φ	2.8	0.7	926	7	25	1.6
386	9	E /	tBuA	0.4 M	H	1.9	0.4	665	٣	.	1.8
387	18	<u> </u>	FOA	0.6 M	н	1.5	0.3%	206	7	m	1.6
388	41	E	FOA	0.6 M	-	27.5	0.6	8328	55	106	3.1
389	q9	<u> </u>	FOA	1.8	~ 1	9.5	\$6.0	2962	27	95	2.7
390	9	ω	MVK	3.0 M	9	1.8	1.3%	626	co	7	1.5
391	9		ы	•	9	10.3		37127		384	3.1
392	q ₉	Δ	/ MA	M 9.0	9	5.0	1.18	1179	13	37	1.8
393	9	A	FOA	1.8 M	7	1.0	5.6%	145	6	18	1.8

9determined by 1H NMR spectroscopy of the non-volatile product fraction; ~0.5 g of Ethylene Copolymers: -100 methyl groups/1000 carbon 386-388: 24 h; Ex CEthylene (E), propylene (P), methyl fDetermined by GPC vs. 389, 37 h); DComplexes 6: {[(2,6-i-PrPh)2DABR2]Pd[CH2CH2CH2CH2C(0)OMe]}BAF (6a); R = Me (6b)); Complexes (FOA), methyl vinyl ketone (MVK) -210 methyl groups/1000 carbon atoms eTurnover number = moles of substrate converted per mole of catalyst. 1: $\{ (2,6-i-PrPh)_2DABR_2 \}$ Pd(Me) (OEt_2) BAF; R = H (1a); R = Me (1b)); acrylate (MA), tert-butyl acrylate (tBuA), H2C=CHC(0)OCH2(CF2)6CF3 ^hBranching: - -67 °C); Propylene Copolymers: volatile products formed additionally; polystyrene standards; atoms (Tg's: mol .

Example 394

Et₂O (30 mL) was added to a round bottom flask containing 445 mg (1.10 mmol) of (2,6-i-PrPh)2DABMe2 and 316 mg (1.15 mmol) of Ni(COD)2. Methyl acrylate (100 μ L) was then added to the flask via microliter syringe. The resulting blue solution was stirred for several hours before the Et₂O was removed in vacuo. The compound was then dissolved in petroleum ether and the resulting solution was filtered and then cooled to -35°C in the drybox freezer. Purple single crystals of 10 [(2,6-i-PrPh)2DABMe2]Ni[H2C=CHCO(OMe)] were isolated: ^{1}H NMR (CD₂Cl₂, 300 MHz, -40°C) δ 7.4 - 7.2 (m, 6, Harvl), 3.74 (br septet, 1, CHMe2), 3.09 (septet, 1, J = 6.75, C'HMe₂), 2.93 (septet, 1, J = 6.75, C''HMe₂), 2.85 (s, 3, 0Me), 2.37 (br septet, 1, C'''HMe2), 2.10 15 (dd, 1, J = 13.49, 8.10, H₂C=CHC(0)OMe), 1.66 (dd, 1, J= 13.49, 4.05, HH'C=CHC(O)OMe), 1.41 (d, 3, J = 6.75, CHMeMe'), 1.35 (dd, 1, J = 8.10, 4.05, HH'C=CHC(O)OMe), 1.26 (d, 3, J = 8.10, C''HMeMe'), 1.24 (d, 3, J = 8.09, C'HMeMe'), 1.13 (d, 3, J = 6.75, C'HMeMe'), 1.09 - 1.03 20 (doublets, 12, CHMeMe', C''HMeMe', C'''HMeMe'), 0.79 and 0.62 (s, 3 each, N=C(Me)-C'(Me)=N); ¹³C NMR (CD₂Cl₂, 300 MHz, -20 °C) δ 174.2 (C(O)OMe), 166.6 and 165.5 (N=C-C'=N), 147.9 and 146.8 (Ar, Ar': Cipso), 139.5, 139.0, 138.2 and 137.7 (Ar: Co, C'o and Ar': Co, 25 C'_{O}), 125.6 and 125.4 (Ar, Ar': C_{D}), 123.5, 123.4, 123.3 and 123.0 (Ar: C_m , C'_m and Ar': C_m , C'_m), 49.9 and $39.8 (H_2C=CHC(0)OMe)$, 28.8, 28.5, 28.4 and 28.3(CHMe₂, C'HMe₂, C''HMe₂, C'''HMe₂), 26.1 $(H_2C=CHC(0)OMe)$, 24.3, 23.8, 23.6, 23.4, 23.0, 22.9, 30 22.7 and 22.7 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 20.21 and 20.16 (N=C(Me)-C'(Me)=N).

Example 395

In a nitrogen-filled drybox, 289 mg (0.525 mmol) of [(2,6-i-PrPh)₂DABMe₂Ni(H₂C=CHCO(OMe))] and 532 mg (0.525 mmol) of H(OEt₂)₂BAF were placed together in a round bottom flask. The flask was cooled in the -35°C freezer before adding 20 mL of cold (-35°C) Et₂O to it.

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The reaction mixture was then allowed to warm to room temperature as it was stirred for 2 h. The solution was then filtered and the solvent was removed in vacuo to yield 594 mg (80.1%) of the 4-membered chelate, {[(2,6-i-PrPh)2DABMe2]Ni[CHMeC(O)OMe]}BAF, as a burnt orange powder: 1 H NMR (CD₂Cl₂, 300 MHz, rt) δ 7.72 (s, 8, BAF: H_O), 7.56 (s, 4, BAF: H_D), 7.5 - 7.2 (m, 6, H_{aryl}), 3.52 (s, 3, OMe), 3.21 (q, 1, J = 6.75, CHMeC(O)OMe), 3.45, 3.24, 3.02 and 3.02 (septet, 1 each, CHMe2, C'HMe2, C''HMe2 and C'''HMe2), 2.11 and 10 2.00 (s, 3 each, N=C(Me)-C'(Me)=N), 1.55, 1.50, 1.47, 1.33, 1.28, 1.24, 1.23 and 1.17 (d, 3 each, CHMeMe', C'HMeMe', C''HMeMe' and C'''HMeMe'), -0.63 (d, 3, J = 6.75, CHMeC(O)OMe); 13 C NMR (CD₂Cl₂, 300 MHz, rt) δ 178.2, 177.0 and 174.1 (C(0) OMe, N=C-C'=N), 162.2 (q, 15 $J_{CB} = 49.7$, BAF: C_{ipso}), 141.2 and 139.8 (Ar, Ar': C_{ipso}), 139.4, 138.89, 138.79 and 138.40 (Ar, Ar': C_{o} , Co'), 135.2 (BAF: Co), 130.0 and 129.6 (Ar, Ar': Cp, C_{D} '), 129.3 (q, BAF: C_{m}), 125.6, 125.2, 125.0 and 124.7 $(Ar, Ar': C_m, C'_m), 125.0 (q, J_{CF} = 272.5, BAF: CF_3),$ 20 117.9 (BAF: Cp), 53.6 (OMe), 30.3, 30.0, 29.9 and 29.8 (CHMe2, C'HMe2, C''HMe2, C'''HMe2), 24.5, 24.1, 24.0, 23.7, 23.33, 23.26, 23.1 and 23.1 (CHMeMe', C'HMeMe', C''HMeMe', C''''HMeMe'), 20.6 and 19.5 (N=C-C'=N), 6.9 25 (CHMeC(O)OMe).

Examples 396-400

Polymerization of ethylene by {[(2,6-i-PrPh)2DABMe2]Ni[CHMeC(0)OMe]}BAF. This compound was used to catalyze the polymerization of polyethylene at temperatures between RT to 80°C. Addition of a Lewis acid often resulted in improved yields of polymer.

General Polymerization Procedure for Examples 396-400. In the drybox, a glass insert was loaded with {[(2,6-i-PrPh)2DABMe2]Ni[CHMeC(O)OMe]}BAF. In addition, 2 equiv of a Lewis acid (when used) was added to the insert. The insert was cooled to -35°C in a drybox freezer, 5 mL of deuterated solvent was added to the cold insert, and the insert was then capped and

sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT or 80°C as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a ¹H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

Example 396

Polymerization Conditions: {[(2,6-i-10 PrPh)2DABMe2]Ni[CHMeC(O)OMe]}BAF (84.8 mg, 0.06 mmol); No Lewis Acid; C6D6; RT. No polymer was isolated and polymer formation was not observed in the ¹H NMR spectrum.

Example 397

Polymerization Conditions: {[(2,6-i-PrPh)2DABMe2]Ni[CHMeC(O)OMe]}BAF (84.8 mg, 0.06 mmol); 2 Equiv BPh3; C6D6, RT. Solid white polyethylene (0.91 g) was isolated.

Example 398

Polymerization Conditions: {[(2,6-i-PrPh)₂DABMe₂]Ni[CHMeC(O)OMe]}BAF (84.8 mg, 0.06 mmol);
Equiv B[3,5-trifluoromethylphenyl]₃; C₆D₆, RT.
Solid white polyethylene (0.89 g) was isolated.

Example 399

Polymerization Conditions: {[(2,6-i-PrPh)₂DABMe₂]Ni[CHMeC(O)OMe]}BAF; 2 Equiv BPh₃; C₆D₆, 80°C. Polyethylene (4.3 g) was isolated as a spongy solid.

Example 400

Polymerization Conditions: {[(2,6-i-PrPh)₂DABMe₂]Ni[CHMeC(O)OMe]}BAF (84.8 mg, 0.06 mmol);
No Lewis Acid; CDCl₃, 80°C. Polyethylene (2.7 g) was isolated as a spongy solid.

Example 401

35 An NMR tube was loaded with $\{[(2,6-i-PrPh)_2DABH_2]NiMe(OEt_2)\}BAF$. The tube was capped with a septum, the septum was wrapped with Parafilm®, and the tube was cooled to -78°C. CD_2Cl_2 (700 μL) and one

equiv of methyl acrylate were added to the cold tube in subsequent additions via gastight microliter syringe. The tube was transferred to the cold NMR probe. Insertion of methyl acrylate and formation of the 4membered chelate complex, {[(2,6-i-PrPh) 2DABH2]Ni[CHEtC(O)OMe] BAF, was complete at -10°C: $1_{
m H~NMR}$ (CD₂Cl₂, 400 MHz, -10°C) δ 8.23 and 8.03 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_O), 7.55 (s, 4, BAF: Hp), 7.5 - 7.2 (m, 6, Haryl), 3.69, 3.51, 3.34 and 3.04 (septet, 1 each, CHMe2, C'HMe2, C''HMe2 and 1.0 $C'''HMe_2$, 3.58 (s, 3, OMe), 1.48, 1.46, 1.46, 1.45, 1.30, 1.27, 1.193 and 1.189 (d, 3 each, J = 6.5 - 7.3, CHMeMe', C'HMeMe', C''HMeMe' and C'''HMeMe'), 0.79 and -0.52 (m, 1 each, CH(CHH'CH₃), 0.68 (t, 3, J = 6.9, $CH(CH_2CH_3)$, (CHEt signal was not assigned due to 15 overlap with other protons).

Example 402

A solution of the 4-membered chelate complex {[(2,6-i-PrPh)₂DABH₂]Ni[CHEtC(O)OMe]}BAF was allowed to stand at RT for 1 day. During this time, conversion to the 6-membered chelate complex, {[(2,6-i-PrPh)₂DABH₂]Ni[CH₂CH₂CH₂C(O)OMe]}BAF, was complete: ¹H NMR (CD₂Cl₂, 400 MHz, rt) δ 8.47 and 8.01 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_O), 7.56 (s, 4, BAF: H_D), 7.5 - 7.0 (m, 6, H_{aryl}), 3.61 (s, 3, OMe), 3.45 and 3.09 (septet, 2 each, CHMe₂ and C'HMe₂), 2.25 (t, 2, J 7.3, CH₂C(O)), 1.61 (pentet, 2, J = 7.3, NiCH₂CH₂CH₂), 1.50, 1.50, 1.46, and 1.30 (d, 6 each, J = 6.8 - 6.9, CHMeMe', C'HMeMe'), 0.92 (t, 2, J = 7.4, NiCH₂).

Examples 403-407

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These Examples illustrate the formation of metallacycles of the formula shown on the right side of the equation, and the use of these metallacycles as polymerization catalysts.

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(R = H, Me, An; M = Ni, Pd)

In the absence of olefin, the ether-stabilized catalyst derivatives were observed to decompose in CD₂Cl₂ solution with loss of methane. catalyst derivative where M = Pd and R = H, methane loss was accompanied by clean and selective formation of the metallacycle resulting from C-H activation of one of the aryl i-propyl substituents. metallacycle could be isolated, although not cleanly, 10 as its instability and high solubility prevented recrystallization. Also it could be converted to another metallacycle in which the diethyl ether ligand is replaced by an olefin ligand, especially ethylene.

Example 403 15

A 700 μ L CD₂Cl₂ solution of {[(2,6-i-PrPh) 2DABH₂] PdMe (OEt₂) }BAF (68.4 mg) was allowed to stand at room temperature for several hours and then at -30°C overnight. Such highly concentrated solutions of 20 the resulting metallacycle wherein R is H and M is Pd were stable for hours at room temperature, enabling 1H and ¹³C NMR spectra to be acquired: ¹H NMR (CD₂Cl₂, 400 MHz, 41 °C) δ 8.17 (s, 2, N=C(H)-C'(H)=N), 7.75 (s, 8, BAF: H_O), 7.58 (s, 4, BAF: H_D), 7.5 - 7.0 (m, 6, H_{aryl}), 3.48 (q, 4, J = 6.88, O(CH_2CH_3)₂), 3.26 (septet, 1, J = 6.49, $CHMe_2$), 3.08 (septet, 1, J =6.86, $C'HMe_2$), 2.94 (septet, 1, J = 6.65, $C''HMe_2$), 2.70 (dd, 1, J = 6.67, 0.90, CHMeCHH'Pd), 2.43 (dd, 1,J = 7.12, 4.28, CHMeCHH'Pd), 2.23 (br m, 1, CHMeCH₂Pd),

1.54 (d, 3, J = 6.86, CHMeCH₂Pd), 1.43 (d, 3, J = 6.79, C''HMeMe'), 1.40 (d, 3, J = 7.12, CHMeMe'), 1.37 (d, 3, J = 6.95, C'HMeMe'), 1.27 (d, 6, J = 6.79, C'HMeMe', C''HMeMe'), 1.12 (d, 3, J = 6.54, CHMeMe'), 1.23 (br m, 6, O(CH₂CH₃)₂), 0.21 (CH₄); ¹³C NMR (CD₂Cl₂, 400 MHz, 5 41 °C) δ 162.5 (J_{CH} = 181.5, N=C(H)), 162.3 (q, J_{BC} = 49.8, BAF: C_{ipso}), 161.2 ($J_{CH} = 178.4$, N=C'(H)), 145.8 and 144.5 (Ar, Ar': Cipso), 141.6, 140.7, 140.3 and 138.8 (Ar, Ar': Cipso), 135.3 (BAF: Co), 131.6 and 129.8 (Ar, Ar': C_p), 129.4 (q, $J_{CF} = 29.9$, BAF: CF_3), 10 128.1, 127.6, 125.2 and 124.5 (Ar, Ar': Co, Co'), 125.1 (BAF: CF₃), 118.0 (BAF: C_p), 72 (br, O(CH₂CH₃)₂), 43.2 (CHMeCH₂Pd), 40.5 (CHMeCH₂Pd), 29.5, 29.1 and 28.8 (CHMe₂, C'HMe₂, C''HMe₂), 26.2 (br), 25.3, 25.2, 25.1, 24.5 (br), 23.3 and 22.1 (CHMeMe', C'HMeMe', C''HMeMe', 15 $CHMeCH_2Pd)$, 15.5 (br, $O(CH_2CH_3)_2$), -14.8 (CH_4).

Example 404

Addition of ethylene to a CD_2Cl_2 solution of the compound prepared in Example 403 resulted in loss of ether and formation of the corresponding ethylene adduct (spectral data: see Example 405.) Warming of the ethylene adduct in the presence of excess ethylene resulted in branched polymer formation: 1.3 ppm $(CH_2)_n$, 0.9 ppm (CH_3) . For the ethylene polymerization initiated by this metallacycle, rates of initiation were significantly slower than rates of propagation.

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Example 405

The metallacycle of Example 403 wherein the diethyl ether ligand was replaced by an ethylene ligand was stable enough so that NMR spectra could be obtained. 1 H NMR (CD₂Cl₂, 400 MHz, -61 °C) $^{\circ}$ C) $^{\circ}$ C 8.25 and 8.23 (N=C(H)-C'(H)=N), 7.74 (s, 8, BAF: H_O), 7.55 (s, 4, BAF: H_D), 7.55 - 7.16 (m, 6, Haryl), 4.67 (m, 2, HH'C=CHH'), 4.40 (m, 2, HH'C=CHH'), 2.95 (septet, 1, J=6.30, CHMe₂), 2.80 (septet, 2, J=6.36, C'HMe₂ and C''HMe₂), 2.53 (br m, 1, CHMeCH₂Pd), 2.43 (d, 1, J=8.16, CHMeCHH'Pd), 1.73 (dd, 1, J=8.16, 2.84, CHMeCHH'Pd), 1.45 and 1.19 (d, 3 each, J=6.79 - 6.40,

CHMeMe'), 1.42 (d, 3, J = 7.05, $CHMeCH_2Pd$), 1.30, 1.30, 1.19 and 0.99 (d, 3 each, J = 6.40 - 6.65, C'HMeMe' and C''HMeMe'); 13 C NMR (CD₂Cl₂, 400 MHz, -61 °C) δ 162.7 $(J_{CH} = 179.7, N=CH), 162.1 (J_{CH} = 180.9, N=C'H), 161.6$ $(q, J_{CB} = 49.7, BAF: C_{ipso}), 144.7, 141.7, 141.2,$ 139.2, 137.5 and 137.1 (Ar, Ar': Cipso, Co, C'o), 134.6 (BAF: Co), 131.0 and 129.0 (Ar, Ar': Cp), 128.6 (q, BAF: C_m), 124.4 (q, $J_{CF} = 272.5$, BAF: CF_3), 124.6 and 124.0 (Ar, Ar': C_m), 117.4 (BAF: C_p), 92.3 (JCH = 162.4, $H_2C=CH_2$), 45.1 (CH_2Pd), 41.1 ($CHMeCH_2Pd$), 28.9, 10 28.5 and 28.2 (CHMe2, C'HMe2, C'HMe2), 26.1, 25.6, 25.1, 24.9, 24.6, 22.9 and 21.4 (CHMeMe', C'HMeMe', C''HMeMe', CHMeCH2Pd).

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Example 406

In a nitrogen-filled drybox, 30 mL of THF was 15 added to a flask containing (2,6-i-PrPh) DABAn (1.87 g, 3.72 mmol) and Ni(COD)₂ (1.02 g, 3.72 mmol). resulting purple solution was stirred for several hours before removing the solvent in vacuo. The product was dissolved in a minimum amount of pentane and the 20 resulting solution was filtered and then placed in the drybox freezer (-35°C) to recrystallize. Purple crystals of [(2,6-i-PrPh)2DABAn]Ni(COD) were isolated (1.33 g, 53.5%, first crop). ¹H NMR (CD₂Cl₂, 300 MHz, rt) δ 7.77 (d, 2, J = 8.06, H_{aryl}), 7.44 (t, 2, J = 25 7.52, H_{aryl}), 7.33 (d, 2, J = 7.70, H_{aryl}), 6.89 (t, 2, $J = 7.70, H_{aryl}$, 6.13 (d, 2, $J = 6.13, H_{aryl}$), 3.93 (br s, 4, COD: -HC=CH-), 3.48 (septet, 4, J = 6.87, CHMe2), 2.54 (br m, 4, COD: -CHH'-), 1.51 (m, 4, COD: -CHH'-), 1.37 (d, 12, J = 6.60, CHMeMe'), 0.77 (d, 12, J30

= 6.60, CHMeMe'); 13 C NMR (CD₂Cl₂, 75.5 MHz, rt) δ 151.7, 151.6, 138.5, 137.1, 133.0, 132.1, 128.8, 125.6, 123.8, 123.7, 119.0 (Caryl), 88.7 (COD: -HC=CH-), 29.9 $(COD: -CH_2-)$, 28.0, 25.1 and 23.8 (CHMeMe').

Example 407

In the drybox, a glass insert was loaded with 35.2 mg (0.0527 mmol) of [(2,6-i-PrPh)2DABAn]Ni(COD) and 55.2 mg (0.0545 mmol) of H(OEt₂)₂BAF. The insert was

cooled to -35°C in the drybox freezer, 5 mL of CDCl3 was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to rt as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a ¹H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene (6.1 g) was isolated and dried under vacuum.

Examples 408-412

(acac)NiEt(PPh3) was synthesized according to published procedures (Cotton, F. A.; Frenz, B. A.; Hunter, D. L. J. Am. Chem. Soc. 1974, 96, 4820-4825).

General Polymerization Procedure for Examples 408-15 In the drybox, a glass insert was loaded with 412. 26.9 mg (0.06 mmol) of (acac)NiEt(PPh3), 53.2 mg (0.06 mmol) of NaBAF, and 0.06 mmol of an α -diimine ligand. In addition, 2 equiv of a phosphine scavenger such as BPh3 or CuCl was sometimes added. The insert was 20 cooled to -35°C in the drybox freezer, 5 mL of C6D6 was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. 25 An aliquot of the solution was used to acquire a 1H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. polyethylene was isolated and dried under vacuum.

Example 408

The α -diimine was $(2,6-i-PrPh)_2DABMe_2$. Solid white polyethylene (1.6~g) was isolated.

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Example 409

The α -diimine was $(2,6-i-PrPh)_2DABMe_2$, and 29.1 mg of BPh₃ was also added. Solid white polyethylene (7.5 g) was isolated.

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Example 410

The α -diimine was $(2,6-i-PrPh)_2DABMe_2$, and 11.9 of CuCl was also added. Solid white polyethylene (0.8 g) was isolated.

Example 411

The α -diimine was $(2,6-i-PrPh)_2DABAn$. Solid white polyethylene $(0.2\ g)$ was isolated.

Example 412

The α -diimine was $(2,6-i-PrPh)_2DABAn$, and 29.1 mg of BPh3 was also added. Solid white polyethylene (14.7 g) was isolated.

Examples 413-420

The following synthetic methods and polymerization procedures were used to synthesize and test the polymerization activity of the functionalized α -diimine ligands of these Examples.

Synthetic Method A. One equiv of glyoxal or the diketone was dissolved in methanol. Two equiv of the functionalized aniline was added to the solution along with ~1 mL of formic acid. The solution was stirred until a precipitate formed. The precipitate was collected on a frit and washed with methanol. The product was then dissolved in dichloromethane and the resulting solution was stirred overnight over sodium sulfate. The solution was filtered and the solvent was removed in vacuo to yield the functionalized α -diimine.

Synthetic Method B. One equiv of glyoxal or the diketone was dissolved in dichloromethane and two equiv of the functionalized aniline was added to the solution. The reaction mixture was stirred over sodium sulfate (~1 week). The solution was filtered and the solvent was removed in vacuo. The product was washed or recrystallized from petroleum ether and then dried in vacuo.

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Nickel Polymerization Procedure. In the drybox, a glass insert was loaded with one equiv each of Ni(COD)₂, H(OEt₂)₂BAF, and the α-diimine ligand. The insert was cooled to -35°C in the drybox freezer; 5 mL of C₆D₆ was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a 1H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

Palladium Polymerization Procedure. In the drybox, a glass insert was loaded with one equiv each of [CODPdMe(NCMe)]BAF and the α -diimine ligand. The insert was cooled to -35°C in the drybox freezer, 5 mL of C_6D_6 was added to the cold insert, and the insert was then capped and sealed. Outside of the drybox, the cold tube was placed under 6.9 MPa of ethylene and allowed to warm to RT as it was shaken mechanically for 18 h. An aliquot of the solution was used to acquire a 1 H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

Example 413

α-Diimine was $(2-\text{hydroxyethylPh})_2\text{DABMe}_2$. Synthetic Method B: ^1H NMR (CDCl₃, 300 MHz, rt) δ 7.28 - 7.20 (m, 4, Haryl), 7.12 (t, 2, J = 7.52, Haryl), 6.67 (d, 2, J = 7.67, Haryl), 3.74 (t, 4, J = 6.79, CH₂OH), 3.11 (br s, 2, OH), 2.76 (t, 4, J = 6.79, CH₂CH₂OH), 2.16 (s, 6, N=C(Me)-C(Me)=N); ^{13}C NMR (CDCl₃, 75 MHz, rt) δ 168.2 (N=C-C=N), 149.0 (Ar: Cipso), 128.4 (Ar: C_O), 130.4, 127.1, 124.6 and 118.2 (Ar: C_m, C_p, C_m', C_O'), 62.9 (CH₂OH), 35.3 (CH₂CH₂OH), 15.8 (N=C(Me)-C(Me)=N).

Nickel Polymerization Procedure: (0.02 mmol scale) Seventy mg of polyethylene was isolated. ¹H

NMR spectrum (C6D6) shows the production of 1- and 2-butenes along with smaller amounts of higher olefins.

Palladium Polymerization Procedure: (0.06 mmol scale) No polymer was isolated, however, the ^1H NMR spectrum shows peaks consistent with the formation of branched polyethylene: 1.3 ppm (CH₂)_n, 0.9 ppm (CH₃ of branches). Broad $\alpha\text{-olefinic}$ resonances are observed in the baseline.

Example 414

10 α -Diimine is $(2,6-\text{Et}-3,5-\text{chloroPh})_2\text{DABMe}_2$. Synthetic Method A: ^1H NMR (CDCl $_3$, 300 MHz, rt) δ 7.19 (s, 1, Haryl), 2.64 (sextet, 4, J = 7.19, CHH'CH $_3$), 2.36 (sextet, 4, J = 7.11, CHH'CH $_3$), 2.10 (s, 6, N=C(Me)-C(Me)=N), 1.05 (t, 12, J = 7.52, CH $_2$ CH $_3$); 13 C NMR (CDCl $_3$, 75 MHz, rt) δ 168.8 (N=C-C=N), 149.3 (Ar: Cipso), 132.3 and 127.4 (Ar: Co and Cm), 124.7 (Ar: Cp), 22.5 (CH $_2$ CH $_3$), 16.8 (N=C(Me)-C(Me)=N), 12.1 (CH $_2$ CH $_3$).

Nickel Polymerization Procedure: (0.06 mmol scale) Solid white polyethylene (14.6 g) was isolated.

Palladium Polymerization Procedure: (0.06 mmol scale) Polyethylene (0.06 g) was isolated as an oil.

1H NMR spectrum (C6D6) shows branched polyethylene along with some internal olefinic end groups.

Palladium Polymerization Procedure: {0.03 mmol scale; Isolated [(2,6-Et-3,5-chloroPh)2DABMe2)]PdMe(NCMe)]BAF was used.}
Polyethylene (2.42 g) was isolated as an oil.

Example 415

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α-Diimine is $(2,6-\text{Et}-3-\text{chloroPh})_2\text{DABMe}_2$. Synthetic Method A: ^1H NMR (CDCl $_3$, 300 MHz, rt) δ 7.10 (d, 2, J = 8.43, Haryl), 7.04 (d, 2, J = 8.07, Haryl), 2.65 (m, 2, CHH'CH $_3$), 2.49 (m, 2, CHH'CH $_3$), 2.30 (m, 4, C'HH'C'H $_3$), 2.08 (s, 6, N=C(Me)-C(Me)=N), 1.15 and 1.07 (t, 6 each, J = 7.52, CH $_2$ CH $_3$ and C'H $_2$ C'H $_3$); 13 C NMR (CDCl $_3$, 75 MHz, rt) δ 168.4 (N=C-C=N), 148.5 (Ar: Cipso), 132.0, 129.1 and 128.6 (Ar: Co, Co', Cm), 126.9

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and 124.3 (Ar: C_m ' and C_p), 24.4 and 22.6 ($C_{12}C_{13}$) and $C_{14}C_{143}$), 16.5 (N=C(Me)-C(Me)=N), 13.4 and 12.4 ($C_{14}C_{13}$) and $C_{14}C_{13}$).

Palladium Polymerization Procedure: {0.03 mmol scale; Isolated [(2,6-Et-3-chloroPh)2DABMe2)PdMe(NCMe)]BAF was used.}

Polyethylene (~1 g) was isolated as an amorphous solid.

Example 416

α-Diimine is (2,6-bromo-4-MePh)₂DABMe₂. Synthetic

10 Method A: ¹H NMR (CDCl₃, 300 MHz, rt) δ 7.40 (m, 4, Haryl), 2.32 (s, 6, Ar: Me), 2.14 (s, 6, N=C(Me)-C(Me)=N); ¹³C NMR (CDCl₃, 75 MHz, rt) δ 171.5 (N=C-C=N), 144.9 (Ar: Cipso), 135.7 (Ar: Cp), 132.4 (Ar: Cm), 112.3 (Ar: Co), 20.2 and 16.9 (N=C(Me)-C(Me)=N and Ar: Me)

Nickel Polymerization Procedure: (0.02 mmol scale) Solid white polyethylene (5.9 g) was isolated. 1H NMR spectrum (C6D6) shows a significant amount of branched polymer along with internal olefinic end groups.

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Palladium Polymerization Procedure: (0.06 mmol scale) Polyethylene (0.38 g) was isolated as an oil. 1H NMR spectrum (C6D6) shows a significant amount of branched polymer along with internal olefinic end groups.

Example 417

 α -Diimine is $(2,6\text{-Me-4-bromoPh})_2\text{DABH}_2$. Synthetic Method A: ^1H NMR (CDCl3, 300 MHz, rt) δ 8.07 (s, 2, N=CH-CH=N), 7.24 (s, 4, Haryl), 2.15 (s, 12, Ar: Me); ^{13}C NMR (CDCl3, 300 MHz, rt) δ 163.6 (N=C-C=N), 148.7 (Ar: Cipso), 131.0 and 128.7 (Ar: Co and Cm), 117.7 (Ar: Cp), 18.1 (Ar: Me).

Nickel Polymerization Procedure: (0.06 mmol scale) Solid white polyethylene (9.5 g) was isolated.

Palladium Polymerization Procedure: (0.06 mmol scale) No polymer was isolated, however, the ^1H NMR spectrum (C6D6) shows the production of $\alpha\text{-}$ and internal olefins (butenes and higher olefins). A small

resonance exists at 1.3 ppm and is consistent with the resonance for $(CH_2)_n$.

Example 418

 α -Diimine is $(2,6\text{-Me-4-bromoPh})_2\text{DABMe}_2$. Synthetic Method A: ^1H NMR (CDCl3, 300 MHz, rt) δ 7.22 (s, 4, Haryl), 2.02 (s, 6, N=C(Me)-C(Me)=N), 2.00 (s, 12, Ar: Me); ^{13}C NMR (CDCl3, 75 MHz, rt) δ 168.5 (N=C-C=N), 147.3 (Ar: Cipso), 130.6 (Ar: C_m), 126.9 (Ar: C_o), 115.9 (Ar: C_p), 17.6 (Ar: Me), 15.9 (N=C(Me)-C(Me)=N).

Nickel Polymerization Procedure: (0.06 mmol scale) Solid white polyethylene (14.9 g) was isolated.

Palladium Polymerization Procedure: (0.06 mmol scale) Polyethylene (1.3 g) was isolated as an oil. The ¹H NMR spectrum (C_6D_6) shows resonances consistent with the formation of branched polymer. Resonances consistent with olefinic end groups are observed in the baseline.

Palladium Polymerization Procedure: {0.03 mmol
scale; Isolated[(2,6-Me-4-

20 bromoPh)₂DABMe₂) PdMe (NCMe)]BAF was used.} Polyethylene (3.97 g) was isolated as a mixture of a soft white solid and an amorphous oil. ¹H NMR spectrum (C₆D₆) shows branched polyethylene.

Example 419

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α-Diimine is (2-Me-6-chloroPh)₂DABMe₂.

Nickel Polymerization Procedure: (0.02 mmol scale) Solid white polyethylene (220 mg) was isolated. In addition, the 1H NMR spectrum (C_6D_6) shows the production of 1- and 2-butenes.

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palladium Polymerization Procedure: $(0.03 \text{ mmol} \text{ scale}; \text{ Isolated } [(2-\text{Me-6-chloroPh})_2\text{DABMe}_2] \text{ PdMe}(\text{NCMe})] \text{SbF}_6 \text{ was used.})$ Polyethylene (3.39 g) was isolated as an oil. The ^1H NMR spectrum (C_6D_6) shows the production of branched polyethylene; internal olefin end groups are also present.

Example 420

(2,6-t-BuPh) 2DABAN

This compound was made by a procedure similar to that of Example 25. Two g (9.74 mmol) of 2,5-di-t-butylaniline and 0.88 g (4.8 mmol) of acenaphthenequinone were partially dissolved in 50 mL of methanol. Attempted crystallization from ether and from CH₂Cl₂ yielded an orange/yellow powder (1.75 g, 66%--not optimized). ¹H NMR (CDCl₃, 250 MHz) δ 7.85 (d, 2H, J = 8.1 Hz, BIAN: H_p), 7.44 (d, 2H, J = 8.4 Hz, Ar: H_m), 7.33 (dd, 2H, J = 8.4, 7.3 Hz, BIAN: H_m), 7.20 (dd, 2H, J = 8.1, 2.2 Hz, Ar: H_p), 6.99 (d, 2H, J = 2.2 Hz, Ar: H_O), 6.86 (d, 2H, J = 7.0 Hz, BIAN: H_O), 1.37, 1.27 (s, 18H each, C(CH₃)₃).

Example 421

A 100mg sample of {[(2,6-i-PrPh)2DABMe2]PdCH2CH2CH2C(0)OCH3}+BAF in a Schlenk flask was dissolved in CH2Cl2 (4ml) and cyclopentene (8ml) added. The flask was flushed well with a 10% ethylene in N2 mix and the solution stirred with a slow flow of the gas mixture passing through the flask. After 15 hours the product had solidified into a single mass of yellow/brown polymer. The reaction was quenched with MeOH and the polymer broken into pieces and washed with MeOH. Yield = 2.0g. DSC: Tm = 165°C (32J/g). Integration of the lh-NMR spectrum indicated 83 mole% cyclopentene.

Example 422

A 37mg sample of [(2,4,6-MePh)2DABAn]NiBr2 in cyclopentene (5ml) was placed in a Schlenk flask under an atmosphere of ethylene. Modified MAO (1.1ml, 7.2wt%

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Al) was added and the reaction allowed to run for 16 hours after which time the product had solidified into a mass of green polymer. The reaction was quenched by addition of MeOH/10%HCl and the polymer was crushed and washed well with MeOH and finally a 2% Irganox/acetone solution. Yield = 3.6g.

Example 423

A 30mg sample of [(2,6-i-PrPh)2DABMe2]NiBr2 was slurried in toluene (2ml) and norbornene (2g). (1ml, 9.6wt% Al) was added. The solution immediately 10 turned deep blue/black and in less than a minute became extremely viscous. The reaction was quenched after 15 hours by addition of MeOH/10%HCl causing the polymer to precipitate. The solid was filtered, washed well with MeOH and finally with a 2% Irganox® 1010 in acetone 15 The polymer was cut into pieces and dried. Yield = 0.8g (40%). ¹H-NMR (ODCB, 120°C): 1.0-2.5 ppm complex multiplet confirms that the product is an addition polymer. The absence of olefinic peaks precludes the existence of ROMP product and indicates 20 that the polymer is not of extremely low molecular weight.

Example 424

A 32mg sample of [(2,6-i-PrPh)2DABMe2]CoCl2 was slurried in toluene (2ml) and norbornene (4g). 25 (1.5ml, 9.6wt% Al) was added. The solution immediately turned deep purple and within a few minutes became extremely viscous and difficult to stir. The reaction was quenched after 4 hours by addition of MeOH/10%HCl causing the polymer to precipitate. The solid was 30 filtered, washed well with MeOH and finally with a 2% Irganox in acetone solution. The polymer was dried overnight at 110°C under vacuum. Yield = 2.1g (53%). It was possible to further purify the product by dissolving in cyclohexane and reprecipitating with 35 1_{H-NMR} (TCE, 120° C): 1.0-2.5 ppm complex multiplet.

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Example 425

A 33mg sample of ((2,4,6-MePh)2DABAn)CoCl2 was slurried in toluene (2ml) and norbornene (4g). PMAO (2.0ml, 9.6wt% Al) was added. The solution immediately turned deep blue and within a few minutes the viscosity began to increase. The reaction was quenched after 4 hours by addition of MeOH/10%HCl causing the polymer to precipitate. The solid was filtered, washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. The polymer was dried overnight at 110°C under vacuum. Yield = 0.8g (13%). It was possible to further purify the product by dissolving in cyclohexane and reprecipitating with MeOH. 1H-NMR (TCE, 120°C): 1.0-2.5 ppm complex multiplet.

Example 426

A 23mg sample of [(2,4,6-MePh)2DABH2]PdMeCl was slurried in toluene (2ml) and norbornene (2.7g). PMAO (1.0mL, 9.6wt% Al) was added. Solids immediately formed and after a few seconds stirring stopped. The reaction was quenched after 2 hours by addition of MeOH/10%HCl. The solid was filtered, crushed and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 2.5g (92%).

Example 427

25 A 16mg sample of [(2,4,6-MePh)2DABH2]NiBr2 was slurried in dicyclopentadiene (~3g). MMAO (1.2ml, 7.2wt% Al) was added. Solution immediately turned deep red/purple and started to foam. The reaction was quenched after 16 hours by addition of MeOH/10%HCl which precipitated the polymer. The solid was filtered and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 0.25g.

Example 428

A 20mg sample of [(2,4,6-MePh)₂DABH₂]PdMeCl was slurried in toluene (2ml) and ethylidene norbornene (2ml). PMAO (1.0mL, 9.6wt% Al) was added. The solution turned a pale orange and after an hour the viscosity had increased. After 14 hours the mixture had

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solidified into a gel and stirring had stopped. The reaction was quenched by addition of MeOH/10%HCl. The solid was filtered, crushed and washed well with MeOH and finally with a 2% Irganox® 1010 in acetone solution. Yield = 0.7g (39%).

Example 429

NiI₂ (0.26g) was placed in THF (10ml) and (2,6-i-prPh)₂DABMe₂ (340mg) was added. The resulting mixture was stirred for 2 days after which the THF was removed and pentane added. The red/brown solid was isolated by filtration and washed several times with pentane. Yield = 0.53g (89%).

A portion of the product (9 mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and 0.25 ml PMAO solution (9.6% Al) was added. The solution turned dark green and, after several hours at room temperature, became viscous. After 16 hours the reaction was quenched with MeOH/10% HCl which precipitated the polymer. The polymer (1.25g) was collected by filtration, washed well with MeOH and dried under reduced pressure. ¹H NMR indicated ~133 methyl per 1000 methylene.

Example 430

CoI₂ (286mg) was dissolved in THF (10ml) and (2,6iPrPh)₂DABMe₂ (370mg) was added. The resulting mixture was stirred for 3 days after which the THF was removed and pentane added. The brown solid was isolated by filtration and washed several times with pentane. Yield = 0.29g (44%). ¹H NMR (THF-d₈) 1.0-1.4 (m, 24H, 30 CH-CH₃), 2.06 (s, 6H, N=C-CH₃), 2.6-2.8 (m, 4H, C-CH-(CH₃)₂), 7.0-7.3 (m, 6H, aromatic). This data is consistent with the formula: [(2,6-iPrPh)₂DABMe₂]CoI₂

A portion of the above product (14mg, 0.02mmol) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and 0.4 ml PMAO solution (9.6% Al) was added. The solution turned purple and, after several hours at room temperature, became viscous. After 18 hours the reaction was

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quenched with MeOH/10% HCl which precipitated the polymer. The polymer (634mg) was collected by filtration, washed well with MeOH and dried under reduced pressure. ¹H NMR indicated ~ 100 methyl per 1000 methylene. DSC: Tg = -45°C.

Example 431

Solid π -cyclooctenyl-1,5-cyclooctadienecobalt (I) (17mg, 0.06mmol) (prepared according to: Gosser L., Inorg. Synth., 17, 112-15, 1977) and solid (2,6iPrPh) 2DABMe2 (24mg, 0.06mmol) were placed in a Schlenk .10 flask and toluene (25mL) added. An ethylene atmosphere was admitted (34 kPa gauge) and the solution stirred for 5 minutes. The final color was brown/green. 0.8 ml PMAO solution (9.6% Al) was added. After 18 hours the reaction was quenched with MeOH/10% HCl which 15 precipitated the polymer. The polymer (190mg) was collected by filtration, washed well with MeOH and dried under reduced pressure. $^{1}\mathrm{H}$ NMR indicated 90 DSC: $Tg = -45^{\circ}C$. methyl per 1000 methylene.

Example 432

[(2,6-iPrPh)₂DABMe₂]CoCl₂ (619mg) was slurried in Et₂O (5ml) and cooled to -25°C. Me₂Mg (63mg in 5ml Et₂O) was added and the solution stirred for 15 minutes. Et₂O was removed under reduced pressure and the resulting bright purple solid was dissolved in pentane, filtered to remove MgCl₂ and the volume reduced to 5 ml. The solution was cooled to -25°C for 2 days and the resulting purple crystals isolated by filtration. Yield = 420mg (73%). Crystal structure determination confirmed that the product was [(2,6-iPrPh)₂DABMe₂]CoMe₂.

[(2,6-iPrPh)₂DABMe₂]CoMe₂ (34mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (140 kPa [absolute]) and after stirring for 2 hours, 0.6 ml PMAO solution (9.6% Al) was added. The solution remained dark purple and, after several hours at room temperature, became viscous. After 48 hours the reaction was quenched with MeOH/10% HCl which

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precipitated the polymer. The polymer (0.838g) was collected by filtration, washed well with MeOH and dried under reduced pressure. Branching ($^{1}H-NMR$): 115 methyl per 1000 methylene. DSC: Tg = $-45^{\circ}C$.

Example 433

[(2,6-iPrPh)₂DABMe₂]CoMe₂ (30mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. Montmorillionite K-10 (Aldrich Chemical Co., Milwaukee, WI, U.S.A.) (200mg, conditioned at 140°C for 48hrs under vacuum) suspended in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 7.5g crystalline polyethylene. Branching (¹H-NMR): 18 Methyl per 1000 methylene.

Example 434

[(2,6-iPrPh)2DABMe2]CoMe2 (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. Montmorillionite K-10 (100mg, conditioned at 600°C for 48hrs under vacuum) suspended in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 3g

polyethylene. Branching (1H NMR): 11 Methyl per 1000 methylene.

Example 435

[(2,6-iPrPh)2DABMe2]CoMe2 (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution

frozen. Tris(pentaflorophenyl)boron (25mg) dissolved in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that

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pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. = 105mg polyethylene. Branching (1H NMR): 60 Methyl per 1000 methylene.

Example 436

[(2,6-iPrPh)2DABMe2]CoMe2 (15mg) was dissolved in benzene (10ml in a shaker tube) and the solution frozen. HBAF 2Et2O (30mg) slurried in benzene (10ml) was added on top of the frozen layer and frozen as well. The solution was thawed under an ethylene atmosphere (6.9 MPa) and shaken at that pressure for 18 hours. MeOH was added to the resulting polymer which was then isolated by filtration, washed well with MeOH and dried under reduced pressure. Yield = 3.8g 15 polyethylene. Branching (1H NMR): 21 Methyl per 1000 methylene.

Example 437

CoCl₂ (102mg) was placed in acetonitrile and AgBF₄ (306mg) added. The solution was stirred for 30 minutes 20 after which the white AgCl was filtered off. (2,6-i-PrPh) 2DABMe2 (318mg) was added and the solution stirred overnight. The acetonitrile was removed under reduced pressure and pentane added. The orange product was isolated by filtration and washed and dried. 25 1.1-1.4 (m, C-CH-CH₃, 24H), 1.8 (CH₃CN, 6H), 2.2 (N=C-CH₃, 6H), 2.7 (m, C-CH-CH₃, 4H), 7.0-7.2 (m, C=CH, 6H). The spectrum is consistent with the molecular formula: [((2,6-

iPrPh) 2DABMe2) Co(CH3CN) 2] (BF4) 2 30

A portion of the product (43mg) in toluene (25mL) in a Schlenk flask was placed under an atmosphere of ethylene (35 kPa gauge) and 0.8 ml PMAO solution (9.6% Al) was added. The solution turned dark purple After 18 hours the reaction was quenched with MeOH/10% HCl which precipitated the polymer. The polymer (0.310g) was collected by filtration, washed well with MeOH and

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dried under reduced pressure. Branching (¹H NMR): 72 Methyl per 1000 methylene.

Example 438

Solid Co(II)[(CH₃)₂CHC(O)O⁻]₂ (17mg, 0.073mmol)

and solid (2,6-iPrPh)₂DABMe₂ (32mg, 0.079mmol) were
placed in a Schlenk flask and toluene (25mL) added. An
ethylene atmosphere was admitted (140 kPa [absolute])
and 3.0 ml PMAO solution (9.6% Al) was added. After 18
hours the reaction was quenched with MeOH/10% HCl which
precipitated the polymer. The polymer (57mg) was
collected by filtration, washed well with MeOH and
dried under reduced pressure. ¹H NMR indicated 32
methyl per 1000 methylene.

Example 439

The complex {[(2,6-EtPh)2DABMe2]PdMe(NCMe)}+SbF6D 15 was weighed (50 mg, 0.067 mmol) into a 100 mL roundbottom flask inside a dry box. Cyclopentene (20 mL, 3400 equivalents per Pd; unpurified) and dichloromethane (20 mL) were added to the flask, and stirred under a nitrogen atmosphere to give a 20 homogeneous solution. A precipitate had formed after 2 After 7 days, the solvent was evaporated and the solids were dried in a vacuum oven to give 0.39 g polymer (86 turnovers/Pd). A sample of the polymer was washed several times with petroleum ether and ether, 25 then dried in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. DSC (0 to 300°C, 10°C/min, first heat): $T_g = 120$ °C, T_m (onset to end) = 179 to 232°C, heat of fusion = 18 J/g. 1H NMR (400 MHz, 120°C, ortho-dichlorobenzene-d4, 30 referenced to solvent peak at 7.280 ppm): 0.905 (bs, 1H, cis -CH-C $\underline{\text{H}}_2$ -CH-), 1.321 (bs, 2H, cis -CH-C $\underline{\text{H}}_2$ -C $\underline{\text{H}}_2$ -CH-), 1.724 and 1.764 (overlapping bs, 4H, trans -CH- CH_2-CH_2-CH- and $-CH-CH_2-CH_2-CH-)$, 1.941 (bs, 1H, trans - $CH-CH_2-CH-)$. The 1H NMR assignments are based upon 2D 35 NMR correlation of the ¹H and ¹³C NMR chemical shifts, and are consistent with a poly(cis-1,3-cyclopentylene) repeat unit.

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Example 440

The complex $\{[(2,6-iPrPh)_2DABAn]PdMe(OEt_2)\}*SbF_6^D$ was weighed (50 mg, 0.054 mmol) into a 100 mL roundbottom flask inside a dry box. Cyclopentene (20 mL, 4200 equivalents per Pd; unpurified) and 5 dichloromethane (20 mL) were added to the flask, and stirred under a nitrogen atmosphere to give a homogeneous solution. A precipitate had formed after 3 days. After 6 days, the solvents were evaporated and the solids were dried in a vacuum oven to give 0.20 g 10 polymer (55 turnovers/Pd). A sample of the polymer was washed several times with petroleum ether and ether, then dried in a vacuum oven. DSC (0 to 300°C, 10° C/min, first heat): $T_g = 42$ °C, T_m (onset to end) = 183 to 242°C, heat of fusion = 18 J/g. 1 H NMR (400 MHz, 70 15 °C, CDCl₃, referenced to solvent peak at 7.240 ppm): 0.75 (bm, 1H, cis -CH-C $\underline{\text{H}}_2$ -CH-), 1.20 (bs, 2H, cis -CH- $CH_2-CH_2-CH-)$, 1.59 and 1.68 (overlapping bs, 4H, trans $-CH-CH_2-CH_2-CH-$ and $-CH-CH_2-CH_2-CH-$), 1.83 (bs, 1H, trans $-CH-CH_2-CH-)$. The ¹H NMR assignments are based 20 upon 2D NMR correlation of the 1H and 13C NMR chemical shifts, and are consistent with a poly(cis-1,3cyclopentylene) repeat unit.

Example 441

The complex [(2,6-iPrPh)₂DABMe₂]PdMeCl was added (28 mg, 0.050 mmol) to a glass vial containing cyclopentene (3.40 g, 1000 equivalents per Pd; distilled twice from Na) inside a dry box. A solution of MMAO in heptane (1.47 mL, 1.7 M Al, 50 equivalents per Pd) was added with stirring to give a homogeneous solution. A precipitate began to form immediately. After 2 days, the solids were collected by vacuum filtration, washed several times on the filter with petroleum ether and ether, then dried in a vacuum oven to give 0.254 g polymer (75 turnovers/Pd). The polymer was pressed at 250°C into a transparent, gray-brown, tough film. DSC (0 to 300°C, 10°C/min, first heat): Tg = 114°C, Tm (onset to end) = 193 to 240°C, heat of

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fusion = 14 J/g. GPC (Dissolved in 1,2,4-trichlorobenzene at 150°C, run in tetrachloroethylene at 100°C, polystyrene calibration): peak MW = 154,000, M_n = 70,200, M_w = 171,000, M_w/M_n = 2.43.

Example 442

The complex $\{(2,6$ $iPrPh)_2DABMe_2]PdCH_2CH_2CH_2C(O)OCH_3$ SbF₆^D was weighed (42) mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene (3.40 g, 1000 equivalents per Pd; distilled twice from Na) and dichloromethane (4.4 mL) 10 were added with stirring to give a homogeneous solution. After 1 day, the solids were collected by vacuum filtration, washed several times on the filter with petroleum ether and ether, then dried in a vacuum oven to give 1.605 g polymer (471 turnovers/Pd). 15 polymer was pressed at 250°C into a transparent, graybrown, tough film. TGA (25 to 600°C, 10°C/min, nitrogen): T_d (onset to end) = 473 to 499, 97.06 % weight loss. TGA (25 to 600 °C, 10 °C/min, air): $T_d =$ 350°C, 5 % weight loss. DSC (0 to 300 °C, 10°C/min, 20 second heat): $T_q = 94$ °C, T_m (onset to end) = 191 to 242 °C, heat of fusion = 14 J/g. GPC (Dissolved in 1,2,4trichlorobenzene at 150°C, run in tetrachloroethylene at 100 °C, polystyrene calibration): peak MW = 152,000, $M_n = 76,000, M_w = 136,000, M_w/M_n = 1.79.$ 25

Example 443

The complex [(2,6-iPrPh)₂DABMe₂]PdCl₂ was weighed (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Pd; distilled from polyphosphoric acid), and the vial was cooled to <0°C. A solution of MMAO in heptane (1.00 mL, 1.7 M Al, 34 equivalents per Pd) was added with stirring to give a homogeneous solution. After 1 day, a copious precipitate had formed. After 2 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, then dried in a vacuum oven to give 1.774 g polymer (520 turnovers/Pd). The polymer was coated with 5000

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ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. DSC (25 to 330°C, 10°C/min, second heat): $T_g = 105$ °C, T_m (onset to end) = 163 to 244° C, heat of fusion = 21 J/g.

Example 444

The complex [(2,6-iPrPh)2DABMe2]PdCl2 was weighed (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Pd; distilled from polyphosphoric acid), and the vial 10 was cooled to <0°C. A solution of EtAlCl2 in hexane (1.7 mL, 1.0 M, 34 equivalents per Pd) was added with stirring to give a homogeneous solution. After 4 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, 15 then dried in a vacuum oven to give 1.427 g polymer (419 turnovers/Pd). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, gray-brown, tough film. 20 (25 to 330°C, 10°C/min, second heat): $T_g = 103$ °C, T_m (onset to end) = 153 to 256° C, heat of fusion = 23 J/g.

Example 445

The complex [(2,6-iPrPh)2DABMe2]PdCl2 was weighed 25 (29 mg, 0.050 mmol) into a glass vial inside a dry box. Cyclopentene was added (6.81 g, 2000 equivalents per Pd; distilled from polyphosphoric acid), and the vial was cooled to <0°C. A solution of EtAlCl2áEt2AlCl in toluene (1.9 mL, 0.91 M, 68 equivalents Al per Pd) was added with stirring to give a homogeneous solution. After 4 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, then dried in a vacuum oven to give 1.460 g polymer (429 turnovers/Pd). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. polymer was pressed at 290°C into a transparent, graybrown, tough film. DSC (25 to 330°C, 10°C/min, second

heat): $T_g = 101$ °C, T_m (onset to end) = 161 to 258°C, heat of fusion = 22 J/g.

Example 446

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed (32 mg, 0.050 mmol) into a glass vial inside a dry box. 5 Cyclopentene was added (6.81 g, 2000 equivalents per Ni; treated with 5 A molecular sieves, and distilled from Na and Ph₃CH), and the vial was cooled to <0°C. A solution of EtAlCl2áEt2AlCl in toluene (1.9 mL, 0.91 M, 68 equivalents Al per Ni) was added with stirring to 10 give a homogeneous solution. After 5 days, the solids were collected by vacuum filtration, washed several times on the filter with ether and cyclohexane, and dried in a vacuum oven to give 2.421 g polymer (711 turnovers/Ni). The polymer was coated with 5000 ppm ... 15 Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, brown, tough film. DSC (25 to 330°C, 10° C/min, second heat): $T_g = 103^{\circ}$ C, T_m (onset to end) = 178 to 272° C, heat of fusion = 22 J/g. 20

Example 447

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed (128 mg, 0.202 mmol) into a glass bottle inside a dry box. Cyclopentene was added (27.1 g, 2000 equivalents per Ni; treated with polyphosphoric acid, and distilled 25 from Na). A solution of EtAlCl₂ in hexane (6.8 mL, 1.0 M, 34 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 1 day, additional cyclopentene was added (58 g, 6200 total equivalents per Ni) to the bottle containing a heavy slurry. 30 5 days, the solids were slurried with ether, collected by vacuum filtration, washed several times with ether and cyclohexane on the filter, and dried in a vacuum oven to give 36.584 g polymer (2660 turnovers/Ni). The polymer was washed with 50:50 aqueous HCl/MeOH, 35 followed by several washings with 50:50 H₂O/MeOH, and dried in a vacuum oven. A fine powder sample was obtained using a 60 mesh screen, and coated with 5000

ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The fine powder was pressed at 290°C into a transparent, pale brown, tough film. TGA (25 to 700°C, 10°C/min, nitrogen): T_d (onset to end) = 478 to 510°C, 99.28 % weight loss. DSC (25 to 330°C, 10°C/min, second heat): $T_g = 101$ °C, T_m (onset to end) = 174 to 279°C, heat of fusion = 25 J/g. DSC (330) to 25°C, 10 °C/min, first cool): T_c (onset to end) = 247 to 142°C, heat of fusion = 28 J/g; T_c (peak) = 223°C. DSC isothermal crystallizations were performed 10 by heating samples to 330°C followed by rapid cooling to the specified temperatures, °C, and measuring the exotherm half-times (min): 200 (1.55), 210 (1.57), 220 (1.43), 225 (< 1.4), 230 (1.45), 240 (1.88), 245 (1.62). DSC thermal fractionation was performed by 15 heating a sample to 330°C followed by stepwise isothermal equilibration at the specified temperatures, °C, and times (hr): 290 (10), 280 (10), 270 (10), 260 (10), 250 (10), 240 (8), 230 (8), 220 (8), 210 (8), 200 (6), 190 (6), 180 (6), 170 (6), 160 (4), 150 (4), 140 20 (4), 130 (3), 120 (3), 110 (3). DSC (25 to 330°C, 10; C/min, thermal fractionation sample): $T_g = 100$ °C; T_m , °C (heat of fusion, J/g) = 128 (0.4), 139 (0.8), 146 (1.1), 156 (1.5), 166 (1.9), 176 (2.1), 187 (2.6), 197 (3.0), 207 (3.2), 216 (3.2), 226 (3.4), 237 (3.6), 25 248 (3.7), 258 (2.3), 269 (1.2), 279 (0.5), 283 (0.1); total heat of fusion = 34.6 J/g. DMA (-100 to 200°C, 1, 2, 3, 5, 10 Hz; pressed film): modulus $(-100 \, ^{\circ}\text{C}) =$ 2500 MPa, γ relaxation = -67 to -70°C (activation energy = 11 kcal/mol), modulus (25°C) = 1600 MPa, α 30 relaxation $(T_g) = 109$ to 110°C (activation energy = 139 kcal/mol).

Example 448

The complex [(2,4,6-MePh)₂DABAn]NiBr₂ was weighed 35 (32 mg, 0.050 mmol) into a glass bottle inside a dry box. Cyclopentene was added (34.1 g, 10,000 equivalents per Ni; high-purity synthetic material distilled from Na), and the vial was cooled to <0°C. A

solution of MMAO in heptane (2.7 mL, 1.95 M Al, 100 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 3 days, a copious precipitate had formed. After 7 days, the reaction was quenched with 20 mL MeOH and 2 mL acetylacetone. The solids were washed several times with 3 mL aqueous HCl in 30 mL MeOH by decanting the free liquids. solids were collected by vacuum filtration, washed several times on the filter with methanol, and dried in a vacuum oven to give 14.365 g polymer (4200 turnovers/Ni). The polymer was coated with 5000 ppm Irganox® 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 290°C into a transparent, colorless, tough film. (0 to 320°C, 20°C/min, second heat): $T_g = 95$ °C, T_m (onset to end) = 175 to 287° C, heat of fusion = 20 J/g.

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Example 449

The complex [(2,4,6-MePh)2DABAn]NiBr2 was weighed (32 mg, 0.050 mmol) into a glass bottle inside a dry box. Cyclopentene was added (34.1 g, 10,000 20 equivalents per Ni; high-purity synthetic material distilled from Na), and the vial was cooled to <0°C. A solution of EtAlCl2áEt2AlCl in toluene (2.8 mL, 0.91 M, 100 equivalents Al per Ni) was added with stirring to give a homogeneous solution. After 3 days, a 25 precipitate had formed. After 7 days, the reaction was quenched with 20 mL MeOH and 2 mL acetylacetone. The solids were washed several times with 3 mL aqueous HCl in 30 mL MeOH by decanting the free liquids. solids were collected by vacuum filtration, washed 30 several times on the filter with methanol, and dried in a vacuum oven to give 7.254 g polymer (2113 turnovers/Ni). The polymer was coated with 5000 ppm Irganox 1010 by evaporating an acetone slurry and drying in a vacuum oven. The polymer was pressed at 35 290°C into a transparent, colorless, tough film. DSC (0 to 320°C, 20°C/min, second heat): $T_q = 94$ °C, T_m (onset to end) = 189 to 274° C, heat of fusion = 18 J/g.

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Example 450

Bis (benzonitrile) palladium dichloride (0.385 g, 1.00 mmol) and (2,6-iPrPh)₂DABMe₂ (0.405 g, 1.00 mmol) were weighed into a glass vial inside a dry box. Dichloromethane (8 mL) was added to give a dark orange solution. Upon standing, the solution gradually lightened in color. Cyclohexane was added to precipitate an orange solid. The solids were collected by vacuum filtration, washed several times with cyclohexane, and dried under vacuum to give 0.463 g (80 10 %) of the complex [(2,6-iPrPh)2DABMe2]PdCl2. 1H NMR (300 MHz, CD₂Cl₂, referenced to solvent peak at 5.32 ppm): 1.19 (d, 12H, CH₃-CHAr-CH₃), 1.45 (d, 12H, CH₃- $CHAr-CH_3$), 2.07 (s, 6H, ($CH_3-C=N-Ar$), 3.07 (m, 4H, $(CH_3)_2$ -CH-Ar), 7.27 (d, 4H, meta ArH), 7.38 (t, 2H, 15 para ArH).

Example 451

A sample of polycyclopentene prepared in a similar fashion to Example 317 gave a transparent, brown, tough film when pressed at 290°C. DSC (25 to 330°C, 10°C/min, 20 second heat): $T_g = 98$ °C, T_m (onset to end) = 174 to 284 $^{\circ}$ C, heat of fusion = 26 J/g. A 5 g sample that was molded at 280°C into a test specimen suitable for an apparatus that measures the response to changes in pressure, volume and temperature, and the data output 25 was used to calculate the following physical properties. Specific gravity, g/cm3, at temperature 1.033 (30), 1.010 (110°C), 0.887 (280), 0.853 (350). Bulk compression modulus, MPa, at temperature 3500 (30), 2300 (110), 1500 (170). The (°C): 30 coefficient of linear thermal expansion was 0.00009 °CD1 between 30 and 110°C.

Example 452

A solution of {[(2,6-i-PrPh)2DABMe2]}
PdCH2CH2CH2C(0)OCH3}+SbF6- (1.703 g) in 1.5 L CH2Cl2
was transferred under nitrogen to a nitrogen purged 1
gallon Hastalloy® autoclave. The autoclave was
charged with 300 g of propylene and stirred for 24 h

while maintaining the temperature at 25°C. The pressure was then vented. The polymer product was floating on the solvent. Most of the solvent was removed in vacuo, and the polymer was dissolved in

- minimal CHCl₃ and then reprecipitated by addition of excess acetone. The polymer was dried in vacuo at 60°C for three days to give 271 g of green rubber.

 Quantitative ¹³C NMR analysis, branching per 1000 CH₂:
- Total methyls (365), \geq Butyl and end of chains (8), 10 CHCH₂CH(CH₃)₂ (31), -(CH₂)_nCH(CH₃)₂ $n\geq$ 2 (25). Based on
- the total methyls, the fraction of 1,3-enchainment is 38%. Analysis of backbone carbons (per 1000 CH₂): δ ⁺ (138), δ ⁺/ γ (1.36).

Listed below are the 13 C NMR data upon which the above analysis is based.

13C NMR data

	TCB, 12	C, 0.05M Cracac
Freq ppm	Intensity	
47.1728	14.6401	
46.7692	9.89618	
46.3285	13.3791	
45.8719	7.94399	
45.4684	11.1421	
45.2719	7.80142	
44.4754	7.11855	
39.1923	29.1488	
38.2791	14.2142	
38.1304	18.7602	
37.9074	14.9366	
37.6631	15.0761	
37.2809	39.5816	
35.5074	8.29039	
34.865	9.75536	
34.5889	14.9541 ·	
34.2915	24.0579	
33.2455	9.86797	
32.9747	19.2516	
30.6013	52.6926	
30.134	55.0735	γ
30.0066	25.1831	Ϋ́
29.7518	144.066	δ+
29.3217	12.2121	3B ₄
28.2013	51.5842	
27.9783	39.5566	
27.5376	33.189	
27.373	35.5457	
27.1659	47.0796	
27.0438	42.1247	

2	25.6315	21.6632	terminal methine			
2	3.3589	15.3063	Methyl of XXVIII	and	XXIX,	2B ₄ ,
			2B ₅ +, 2EOC			
2	23.0722	18.4837	Methyl of XXVIII	and	XXIX,	2B ₄ ,
			2B ₅ +, 2EOC			
2	22.5306	77.0243	Methyl of XXVIII	and	XXIX,	$2B_4$,
		,	2B ₅ +, 2EOC			•
2	21.1129	7.78367				
2	20.5554	26.9634	1B ₁			
2	20.4386	30.3105	1B ₁			
2	20.0085	22.478	1B ₁			
1	19.743	46.6467	1B ₁			
1	13.8812	9.03898	1B ₄ +, 1EOC			

Example 453

A 250 mL Schlenk flask was charged with 10 mg of [(2,6-i-PrPh)2DABH₂]NiBr₂ (1.7x10⁻⁵ mol), and 75 mL of dry toluene. The flask was cooled to 0°C and filled with propylene (1 atm) before addition of 1.5 mL of a 10% MAO solution in toluene. After 45 min, acetone and water were added to quench the reaction. polypropylene was recovered from the flask and washed with 6 M HCl, H_2O , and acetone. The resulting polymer 10 was dried under high vacuum overnight to yield 1.2 g (2300 TO/h) polypropylene. Differential scanning calorimetry: Tg = -19°C. GPC (trichlorobenzene, 135° C, polystyrene reference): Mn = 32,500; Mw = 60,600; Mw/Mn = 1.86. Quantitative ¹³C NMR analysis, branching 15 Based on the total per 1000 CH2: Total methyls (813), methyls, the fraction of 1,3-enchainment is 7%. Analysis of backbone carbons (per 1000 CH_2): δ^+ (3), $\delta + / \gamma$ (0.4).

20 Listed below are the ¹³C NMR data upon which the above analysis is based.

13C NMR data

	TCB,	120C,	0.05M	Cracac
Freq ppm				Intensity
47.194				18.27
46.9922			•	21.3352
46.8276				35.7365
46.2011				27.2778
45.4153				8.55108
43.5356				2.71929
42.925			•	3.37998

41.5551	2.63256
38.826	3.03899
38.4012	10.2858
38.0561	8.50185
37.626	7.10732
37.4879	6.55335
37.2755	9.25058
36.1021	4.48005
35.3057	14.5319
34.4986	11.1193
33.219	9.43548
32.9375	4.94953
32.242	3.16177
308349	24.1766
30.5217	19.8151
30.0916	3.70031
28.1111	144
27.5217	13.9133
27.1394	3.83857
24.5005	6.94946
21.0439	5.25857
20.5342	40.8641
20.0191	60.4325
19.8758	63.0429
16.9236	6.47935
16.3926	5.92056
14.9006	10.6275
14.513	3.39891
•	

Example 454

Preparation of (2-t-BuPh) 2DABAn. A Schlenk tube was charged with 2-t-butylaniline (3.00 mL, 19.2 mmol)

and acenaphthenequinone (1.71 g, 9.39 mmol). The reagents were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. An orange solid formed and was collected via filtration after stirring

overnight. The solid was crystallized from CH₂Cl₂ (3.51 g, 84.1%). ¹H NMR (CDCl₃, 250 MHz) & 7.85 (d, 2H, J = 8.0 Hz, BIAn: H_p), 7.52 (m, 2H, Ar: H_m), 7.35 (dd, 2H, J = 8.0, 7.3 Hz, BIAn: H_m), 7.21 (m, 4H, Ar: H_m and H_p), 6.92 (m, 2H, Ar: H_o), 6.81 (d, 2H, J = 6.9 Hz, BIAn: H_o), 1.38 (s, 18H, C(CH₃)₃).

Example 455

Preparation of $(2,5-t-BuPh)_2DABAn$. A Schlenk tube was charged with 2,5-di-t-butylaniline (2.00 g, 9.74 mmol) and acenaphthenequinone (0.88 g, 4.8 mmol). The

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reagents were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. A solid was collected via filtration after stirring overnight. Attempted crystallization from ether and from CH₂Cl₂ yielded an orange/yellow powder (1.75 g, 66%. ¹H NMR (CDCl₃, 250 MHz) δ 7.85 (d, 2H, J = 8.1 Hz, BIAn: H_p), 7.44 (d, 2H, J = 8.4 Hz, Ar: H_m), 7.33 (dd, 2H, J = 8.4, 7.3 Hz, BIAn: H_m), 7.20 (dd, 2H, J = 8.1, 2.2 Hz, Ar: H_p), 6.99 (d, 2H, J = 2.2 Hz, Ar: H_o), 6.86 (d, 2H, J = 7.0 Hz, BIAn: H_o), 1.37, 1.27 (s, 18H each, C(CH₃)₃).

Example 456

Preparation of [(2-t-BuPh)2DABAn]NiBr2. A Schlenk tube was charged with 0.202 g (0.454 mmol) of (2-t-BuPh)2DABAn, which was then dissolved in 15 mL of CH2Cl2. This solution was cannulated onto a suspension of (DME)NiBr2 (0.135 g, 0.437 mmol) in 10 mL of CH2Cl2. The reaction mixture was allowed to stir overnight resulting in a deep red solution. The solution was filtered and the solvent evaporated under vacuum. The residue was washed with ether (2x10 mL) and an orange/rust solid was isolated and dried under vacuum (0.18g, 62%).

Example 457

Preparation of [(2,5-t-BuPh)2DABAn]NiBr2. A Schlenk tube was charged with 0.559 g (1.00 mmol) of (2,5-t-BuPh)2DABAn, 0.310 g (1.00 mmol) of (DME)NiBr2 and 35 mL of CH2Cl2. The reaction mixture was allowed to stir overnight. The solution was filtered and the solvent evaporated under vacuum. The residue was washed with ether and resulted in an orange solid which was dried under vacuum (0.64 g, 83%).

Example 458

Preparation of highly chain-straightened polypropylene with a low Tg. The complex [(2-t-BuPh)2DABAn]NiBr2 (0.0133g, 2.0x10⁻⁵ mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and backfilled with propylene. Freshly distilled toluene (100

mL) was added via syringe and the resulting solution was stirred in a water bath at room temperature. Polymerization was initiated by addition of methylaluminoxane (MAO; 1.5 mL 10% soln in toluene) and a propylene atmosphere was maintained throughout the course of the reaction. The reaction mixture was stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected, washed with water and acetone, and dried under vacuum. Yield = 1.41 g. DSC: T_{c} -53.6°C, T_{m} -20.4°C (apparent Tm is a small shoulder on the Tg). Quantitative 13 C NMR analysis, branching per 1000 CH2: Total methyls (226), ≥Butyl and end of chains (8.5), CHCH2CH(CH3)2 (2.3), - $(CH_2)_nCH(CH_3)_2$ $n\geq 2$ (12.1). Based on the total 15 methyls, the fraction of 1,3-enchainment is 53%. Analysis of backbone carbons (per 1000 CH2): δ^+ (254), δ^{+}/γ (1.96).

Example 459

Preparation of highly chain-straightened 20 polypropylene with a low T_{Q} . The complex [(2,5-t- $BuPh)_2DABAn]NiBr_2$ (0.0155g, 2.0x10⁻⁵ mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and 25 the resulting solution was stirred in a water bath at room temperature. Polymerization was initiated by addition of 1.5 mL of a 10% MAO solution in toluene, and a propylene atmosphere was maintained throughout the course of the reaction. The reaction mixture was 30 stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected, washed with water and acetone, and dried under vacuum. Yield = 0.75 g. DSC: T_q -53.0°C, T_m none observed. 35 Quantitative 13C NMR analysis, branching per 1000 CH₂: Total methyls (307), \geq Butyl and end of chains (11.2), -CHCH₂CH(CH₃)₂ (11.5), -(CH₂)_nCH(CH₃)₂, $n \ge 2$ (5.9). Based

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on the total methyls, the fraction of 1,3-enchainment is 43%.

Listed below are the $^{13}\mathrm{C}$ NMR data upon which the above analysis is based.

13_C NMR data

		0.05M CrAcAc
Freq ppm	Intensity	
46.3126	6.77995	• .
46.079	6.56802	
45.463	7.82411	
45.2453	6.98049	
39.1764	8.95757	
38.4384	5.42739	
38.1145	20.5702	
37.8755	18.8654	
37.626	19.2917	
37.2702	128.202	
35.0773	6.30042	
34.5304	19.5098	
34.2543	38.6071	
33.7818	4.3205	
33.2986	16.3395	•
32.9588	72.1002	
31.934	10.626	•
31.419	5.57124	,
30.5907	41.727	
30.1287	134.312	γ
29.7518	351.463	δ+
29.3217	9.58971	
28.1589	21.1043	
27.9677	17.7659	
27.5589	44.1485	
27.3783	25.0491	
27.1766	119.562	
27.0226	52.4586	
~25.6		terminal methine of XXVIII
24.5908	8.69462	
24.4315	9.27804	· · · · · · · · · · · · · · · · · · ·
22.5253	30.7474	region of methyls of XXVIII
		and XXIX, 2B ₄ +, 2EOC
20.4333	20.0121	1B ₁
19.7271	103.079	1B ₁
14.7679	5.0022	
14.4068	4.56246	
13.8812	12.3077	1B ₄ +, 1EOC

Example 460

Preparation of highly chain-straightened poly-1- 10 hexene with a high T_m . A flame-dried 250 mL Schlenk flask under a nitrogen atmosphere was charged with 40 mL of freshly distilled toluene, 0.0133 g of [(2-t-

BuPh) 2DABAn] NiBr2 (2.0x10⁻⁵ mol), 5.0 mL of 1-hexene, and 55 mL more toluene (100 mL total volume of liquid). Polymerization was initiated by addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture was stirred for 11.5 hours at room temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 1.84 g. DSC: Tg -44.8°C, Tm 46.0°C.

Example 461

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Preparation of highly chain-straightened poly-1-hexene with a high T_m. A flame-dried 250 mL Schlenk flask under a nitrogen atmosphere was charged with 40 mL of freshly distilled toluene, 0.0155g of [(2,5-t-BuPh)2DABAn]NiBr2 (2.0x10⁻⁵ mol), 5.0 mL of 1-hexene, and 55 mL more toluene (100 mL total volume of liquid). Polymerization was initiated by addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture was stirred for 11.5 hours at room temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 1.07 g. DSC: Tg -54.7°C, Tm 12.5°C.

Example 462

Preparation of [(2-t-BuPh)2DABAn]PdMe2 from (1,5-cyclooctadiene)PdMe2. The Pd(II) precursor (1,5-cyclooctadiene)PdMe2 ((COD)PdMe2) was prepared according reported procedures (Rudler-Chauvin, M.; Rudler, H. J. Organomet. Chem., 1977, 134, 115.) and was handled using Schlenk techniques at temperatures of -10°C or below. A flame-dried Schlenk tube was charged with 0.056 g (0.229 mmol) of (COD)PdMe2 and cooled to -40°C in a dry ice/isopropanol bath. The solid was dissolved in 10 mL of ether, and the diimine (2-t-BuPh)2DABAn (0.106 g, 0.238 mmol) was cannulated onto the stirring solution as a slurry in 15 mL of ether.

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The reaction was warmed to 0 °C and stirring was continued for two hours. The reaction flask was stored at -30°C for several days and resulted in the formation of a green precipitate which was isolated via The supernatant was pumped dry under high filtration. vacuum and also resulted in a green solid. Both solids were determined to be [(2-t-BuPh)2DABAn]PdMe2 by 1H NMR spectroscopy. Isolated yield = 0.083 g (0.143 mmol, 62.4%).

Example 463

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88.7%).

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10 Preparation of [(2,5-t-BuPh)2DABAn]PdMe2 from (1,5-cyclooctadiene) PdMe2. The Pd(II) precursor (1,5cyclooctadiene)PdMe2 ((COD)PdMe2) was prepared according reported procedures (Rudler-Chauvin, M.; Rudler, H. J. Organomet. Chem., 1977, 134, 115.) and 15 was handled using Schlenk techniques at temperatures of -10°C or below. A flame-dried Schlenk tube was charged with 0.102 g (0.417 mmol) of (COD)PdMe2 and cooled to -30°C in a dry ice/isopropanol bath. The solid was dissolved in 10 mL of ether, and the diimine (2,5-t-20 BuPh) 2DABAn (0.234 g, 0.420 mmol) was cannulated onto the stirring solution as a slurry in 40 mL of ether. The reaction was warmed to 0°C and stirring was continued for four hours. The reaction flask was stored at -30°C overnight. The resulting dark green 25 solution was filtered and the solvent was pulled off under high vacuum to give a dark green powder. Analysis by 1H NMR spectroscopy showed the solid to be consistent with the desired product, [(2,5-t-BuPh) $_2$ DABAn] PdMe $_2$. Yield = 0.256 g (0.370 mmol, 30

Example 464

In a dry box, polymer from Example 469 (0.57 g), THF (10.10 g) and acetic anhydride (0.65 g) were placed in a 20 mL vial equipped with a stirring bar. After one hour at room temperature, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water and ether. The organic phase

was separated, washed with water (2x), dried over anhydrous sodium sulfate, concentrated at reduced pressure and then dried under vacuum, affording 4.44 g of polymer. GPC analysis (PS STD.): Mn = 17600, Mw = 26000, PD = 1.48.

Example 465

Preparation of CH₂=CH(CH₂)₂CHICH₂(CF₂)₂OCF₂CF₂SO₂F

A mixture of 72 g of hexadiene, 127.8 g of

ICF₂CF₂OCF₂CF₂SO₂F, 7.0 g of Cu powder and 180 mL of

10 hexane was stirred at 90°C overnight. Solids were

removed by filtration and washed with hexane. After

removal of volatiles, residue was distilled to give

115.3 g of product, bp 80°C/210 Pa. ¹⁹F NMR: +45 (t, J =

6.0 Hz, 1F), -82.7 (m, 2F), -88.1 (dt, J = 42.5 Hz, J =

12.6 Hz, 1F), -88.7 (dt, J = 45.5 Hz, J = 12.6 Hz, 1F),

-112.7 (m, 2F), -115.9 (ddd, J = 2662.2 Hz, J = 30.0

Hz, J = 8.2 Hz, 1F), -118.9 (ddd, J = 262.2 Hz, J =

26.8 Hz, J = 7.4 Hz, 1F).

Example 466

Preparation of CH₂=CH(CH₂)₄ (CF₂)₂OCF₂CF₂SO₂F 20 To a stirred solution of 100 g of $CH_2=CH(CH_2)_2CHICH_2(CF_2)_2OCF_2CF_2SO_2F$ and 200 mL of ether was added 63 g of Bu₃SnH at room temperature. After the addition was complete, the reaction mixture was refluxed for 4 hours and then cooled with ice water. 25 Excess of Bu₃SnH was destroyed by addition of iodine. After being diluted with 200 mL of ether, the reaction mixture was treated with a solution of 25 g of KF in 200 mL of water for 30 min. The solids were removed by filtration through a funnel with silica gel and washed 30 with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried over MgSO4. After removal of the ether, residue was distilled to give 54.7 g of product, bp 72° C/1.3 kPa, and 12.2 g of starting material. 35

Example 467

Preparation of $CH_2=CH(CH_2)_4(CF_2)_4OCF_2CF_2SO_2F$ A mixture of 24 g of hexadiene, 53 g of $I(CF_2)_4OCF_2CF_2SO_2F$, 3.0 g of Cu powder and 60 mL of hexane was stirred at $70^{\circ}C$ overnight. Solids were removed by filtration and washed with hexane. After removal of volatiles, residue was distilled to give 115.3 g of adduct, $CH_2=CH(CH_2)_2CHICH_2(CF_2)_4OCF_2CF_2SO_2F$, bp $74^{\circ}C/9$ Pa. ¹⁹F NMR: +45.5 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -112.2 (dm, J = 270 Hz, 1F), -112.6 (m, 2F), -115.2 (dm, J = 270 Hz, 1F), -124.3 (s, 2F), -125.5 (m, 2F).

To stirred solution of 47 g of CH₂=CH(CH₂)₂CHICH₂(CF₂)₄OCF₂CF₂SO₂F and 150 mL of ether was added 27 g of Bu₃SnH at room temperature. After the addition was complete, the reaction mixture was stirred overnight. Excess of Bu₃SnH was destroyed by addition of iodine. After being diluted with 150 mL of ether, the reaction mixture was treated with a solution of 20 g of KF in 100 mL of water for 30 min. The solids were removed by filtration through a funnel with silica gel and washed with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried over MgSO₄. After removal of the ether, residue was distilled to give 24.7 g of product, bp 103°C/1.3 kPa. 19 F NMR: +45.4 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -.112.6 (t, J = 2.6 Hz, 2F), -115.1 (t, J = 15 Hz, 2F), -124.3 (s, 2F), -125.7 (t, J = 14 Hz, 2F). HRMS: calcd for $C_{12}H_{11}F_{13}SO_3$: 482.0221. Found: 482.0266.

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Example 468

Hydrolysis of Copolymer

Copolymer containing 8.5 mol% of comonomer (1.5 g) was dissolved in 30 mL of THF at room temperature. KOH (0.5 g) in 5 mL of ethanol and 3 mL of water was added and the resulting mixture was stirred at room temperature for six hours. After removal of the solvent, residue was treated with diluted HCl for 70 hours and then filtered to give solids which were

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washed with water, HCl and dried under full vacuum at 70°C for two days to give 1.4 g solid.

Example 469

Hydrolysis of Copolymer

A mixture of 10.6 g of copolymer 5.0 g of KOH, 2 mL of water, 30 mL of ethanol and 30 mL of THF was stirred at room temperature overnight and at 60 to 70°C for 5 hours. After removal of a half of solvents, residue was treated with Conc. HCl to give rubbery material, which was poured into a blender and blended with water for 30 min. Filtration gave solids, which were washed with conc. HCl, and water and dried under vacuum at 60°C overnight to give 8.7 g of dark rubbery material. 19F NMR(THF): -82.8 (br, 2F), -88.5 (br, 2F), -118.3 (br, 2F), -118.5 (br, 2F).

Example 470

Hydrolysis of Homopolymer

A solution of 2.0 g of KOH in 25 mL of ethanol and 2 mL of waster was added to a flask with 3.0 g of homopolymer. The resulting heterogeneous mixture was stirred at room temperature overnight and heated to 60°C for 2hours. After removal of one-half of liquid, the reaction mixture treated with 40 mL of conc. HCl for 30 min. Filtration gave white solids which were washed with conc. HCl, and distilled water and dried under vacuum at 60-70°C for 24 hours to give 2.9 g of white powder.

Example 471

1-Octadecene (8 mL, 8 vol %) was added to a suspension of $[(2,6-i-PrPh)_2DABAn]NiBr_2$ (12 mg, 1.7x10⁻⁵ mol) in 100 mL of dry toluene. The flask was cooled to -1°C using an Endocal® refrigerated circulating bath and 2.5 mL of a 7% MMAO solution in heptane was added. After stirring the reaction for 40 min, the flask was filled with propylene (1 atm) and stirred for 20 35 The propylene was removed in vacuo and the minutes. reaction allowed to continue for an additional 40 min. Acetone and water were added to quench the

polymerization and precipitate the polymer. The resulting triblock polymer was dried under high vacuum overnight to yield 650 mg of a rubbery solid. GPC (trichlorobenzene, 135 °C, polystyrene reference): $M_{\rm n}$ = 60,100; $M_{\rm w}$ = 65,500; $M_{\rm w}/M_{\rm n}$ = 1.09. DSC analysis: Two melt transitions were observed. $T_{\rm m}$ = 8°C (32 J/g), $T_{\rm m}$ = 37°C (6.5 J/g). ¹H-NMR analysis (CDCl₃): signals attributable to repeat units of propylene and 1-octadecene were observed.

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Example 472

Preparation of (2-i-Pr-6-MePh) 2DABAn

A Schlenk tube was charged with 2-isopropyl-6-methylaniline (5.00 mL, 30.5 mmol) and acenaphthenequinone (2.64 g, 14.5 mmol). The reagents were partially dissolved in 50 mL of methanol (acenaphthenequinone was not completely soluble) and 1-2 mL of formic acid was added. An orange/yellow solid was collected via filtration after stirring overnight, and was washed with methanol and dried under vacuum.

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Example 473

Preparation of (2-i-Pr-6-MePh) 2DABMe2

A Schlenk tube was charged with 2-isopropyl-6-methylaniline (5.00 mL, 30.5 mmol) and 2,3-butanedione (1.31 mL, 14.9 mmol). Methanol (5 mL) and one drop of concentrated HCl were added and the mixture was heated to reflux with stirring for 30 minutes. The methanol and remaining dione were removed under vacuum to give a dark, oily residue. The oil was chromatographed on a silica gel column using 10% ethyl acetate: 90% hexane as the eluent. The fractions containing the pure dimine were combined and concentrated. The remaining solvents were removed under vacuum to give a pale yellow powder (0.9217 g, 17.75 %).

Example 474

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Preparation of [(2-i-Pr-6-MePh)2DABAn]NiBr2
Under inert conditions, a flame-dried Schlenk tube
was charged with 0.50 g (1.13 mmol) of (2-i-Pr-6MePh)2DABAn, 0.34 g (1.10 mmol) of (DME)NiBr2 and 25 mL

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of CH_2Cl_2 . The reaction mixture was allowed to stir overnight. The solution was filtered and the solvent removed under vacuum. The residue was washed with ether (4 x 10 mL) to give an orange/yellow powder which was dried under vacuum overnight (0.68 g, 94%).

Example 475

Preparation of [(2-i-Pr-6-MePh) 2DABMe2] NiBr2
Under inert conditions, a flame-dried Schlenk tube
was charged with 0.3040 g (0.8722 mmol) of (2-i-Pr-6MePh) 2DABMe2, 0.2640 g (0.8533 mmol) of (DME) NiBr2 and
25 mL of CH2Cl2. The reaction mixture was allowed to
stir overnight. A solid was collected via filtration
and washed with ether (2 x 10 mL). Upon sitting, more
solid precipitated from the supernatant. This
precipitate was isolated via filtration, washed with
ether, and combined with the originally isolated
product. The combined yellow/orange solids were dried
under vacuum overnight (0.68 g, 94%).

Example 476

Under a nitrogen atmosphere, the complex [(2-i-Pr-20 6-MePh) 2DABAn] NiBr2 (0.0099 g, 1.5x10⁻⁵ mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and the resulting solution was stirred for five minutes at 25 room temperature. Polymerization was initiated with addition of methylaluminoxane (MAO; 1.5 mL 10% solution in toluene) and a propylene atmosphere was maintained The reaction throughout the course of the reaction. was stirred for two hours at constant temperature, at 30 which point the polymerization was by quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, washed with water and acetone, and dried under vacuum. Yield = 3.09 g. DSC: 31.2°C. GPC: $M_n = 142,000$; $M_w = 260,000$; $M_w/M_n = 142,000$ 35 1.83.

Example 477

Under a nitrogen atmosphere, the complex [(2-i-Pr-6-MePh) 2DABMe2] NiBr2 (0.0094 g, 1.5x10-5 mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and the resulting solution was stirred for five min at room temperature. Polymerization was initiated with addition of methylaluminoxane (MAO; 1.5 mL 10% solution in toluene) and a propylene atmosphere was maintained throughout the course of the reaction. reaction was stirred for two hours at constant temperature, at which point the polymerization was by quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, washed with water and acetone, and dried under vacuum. Yield = 1.09 g. DSC: $T_q - 36.1$ °C. GPC: $M_n = 95,300$; $M_w = 141,000$; $M_{\rm W}/M_{\rm n} = 1.48.$

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Example 478

Under a nitrogen atmosphere, a flame-dried 250 mL 20 Schlenk flask was charged with 40 mL of freshly distilled toluene, 0.0133 g $(2.0 \times 10^{-5} \text{ mol})$ of [(2-i-Pr-6-MePh) 2DABAn] NiBr2, 10.0 mL of 1-hexene, and 50 mL more toluene (100 mL total volume of liquid). mixture was stirred in a room temperature water bath 25 for 10 minutes and polymerization was initiated with addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture was stirred for one hour at room temperature and was quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone, 30 collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 3.23 g. DSC: Tg -58.0°C, Tm -16.5°C.

Example 479

35 Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 40 mL of freshly distilled toluene, 0.0125 g (2.0x10⁻⁵ mol) of [(2-i-Pr-6-MePh)2DABMe2]NiBr2, 10.0 mL of 1-hexene, and 50 mL

more toluene (100 mL total volume of liquid). The mixture was stirred in a room temperature water bath for 10 min and polymerization was initiated with addition of 2.0 mL of MAO (10% solution in toluene). The reaction mixture was stirred for 22 h at room temperature and was quenched with 6M HCl. Polymer was precipitated from the resulting solution with acetone,

collected via filtration, washed with water and acetone, and dried under vacuum. Yield = 2.10 g. DSC:

10 T_q -56.4°C, T_m 0.2°C.

Example 480

Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 40 mL of freshly distilled toluene, 0.0133 g (2.0×10^{-5} mol) of [(2-t-BuPh) 2DABAn] NiBr2, 10.0 mL of 1-hexene, and 50 mL more 15 toluene (100 mL total volume of liquid). The mixture was stirred in an isopropanol bath maintained at approximately -10 to -12 C, and polymerization was initiated with addition of 2.5 mL of MMAO (7.2% solution in heptane). The reaction mixture was stirred 20 for two hours at constant temperature and was quenched with acetone/water/6M HCl. The mixture was added to acetone to precipitate the polymer. After settling overnight the polymer was collected via filtration, washed with water and acetone, and dried under vacuum. 25 Yield = 0.35 g. DSC: (two broad melt transitions observed) $T_m(1)$ 34.3°C, $T_m(2)$ 66.4°C. Based on the $^1\mathrm{H}$ NMR spectrum, the polymer contains 41 methyl branches/1000 carbons (theoretical = 55.5 Me/1000 C), indicating a high degree of chain straightening. 30

Example 481

Under a nitrogen atmosphere, a flame-dried 250 mL Schlenk flask was charged with 25 mL of freshly distilled toluene, 0.0133 g (2.0x10⁻⁵ mol) of [(2-t-BuPh)2DABAn]NiBr2, 63 mL more toluene, and 12.0 mL of 1-octadecene (100 mL total volume of liquid). The flask was cooled to -10°C in a CO2/isopropanol bath and stirred at this temperature for several minutes. The

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temperature was maintained at approximately -10°C throughout the reaction by continually adding dry ice as needed. Polymerization of 1-octadecene was initiated with addition of 2.5 mL of MMAO (7.2% solution in heptane). At 2 h, 10 min the reaction flask was twice evacuated and back-filled with propylene. The polymerization was stirred under one atmosphere of propylene for 20 min. The propylene was removed by repeatedly evacuating the flask and backfilling with argon until propylene evolution from the 10 solution was no longer apparent. The polymerization was allowed to continue stirring in the presence of the remaining 1-octadecene until a total elapsed time of five hours was reached. The reaction was quenched with acetone/water/6M HCl. Polymer was precipitated in 15 methanol/acetone, collected via filtration, washed with water and acetone, and dried under vacuum. Yield = T_g 8.0°C, T_m 53.3°C. GPC: M_n = 55,500; 1.03 g. DSC: $M_W = 68,600$; $M_W/M_D = 1.24$. It is believed a block copolymer was formed. 20

Example 482

Preparation of [(2-t-BuPh)2DABAn]PdMe(Et2O)BAF-Under inert conditions, a flame-dried Schlenk tube was charged with 0.1978 g $(3.404 \times 10^{-4} \text{ mol})$ of [(2-t-25 BuPh) 2DABAn] PdMe2 and 0.3451 g (3.408x10-4 mol) of H+(Et₂O)₂BAF-. The Schlenk tube was cooled to -78°C and 10 mL of ether was added. The Schlenk tube was transferred to an ice water bath and the reaction was stirred until the solids were dissolved and the color of the solution became deep red. The ether was then removed under vacuum to give a red, glassy solid that was crushed into a powder (yield was quantitative).

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Example 483

Preparation of [(2,5-t-BuPh)2DABAn]PdMe(Et20)BAF-Following the procedure of Example 482, a red solid with the structure [(2,5-t-BuPh) 2DABAn] PdMe (Et2O) BAF was obtained (quantitative yield).

Example 484

Preparation of [(2-t-BuPh)2DABMe2]PdMe(NCMe)BAF-Under inert conditions, a flame-dried Schlenk tube was charged with 0.1002 g (0.378 mmol) of (COD)PdMeCl and 0.3348 g (0.378 mmol) of NaBAF. The Schlenk tube was cooled to -30°C and 25 mL of CH2Cl2 and 0.10 mL of NCMe were added via syringe. The reaction was stirred for two h at -20 to -30°C. The resulting colorless solution was filtered into another cooled Schlenk tube, 20 mL of hexane was added, and the solvents were 10 removed under vacuum to give a white powder [isolated (COD) PdMe (NCMe) BAF-]. This cationic precursor was combined with 0.138 g (0.396 mmol) of (2-t-BuPh) DABMe2 in 50 mL of NCMe. The reaction mixture was stirred overnight at room temperature. The solution was 15 filtered and extracted with hexane (3 \times 10 mL), and the solvents were removed under vacuum. The resulting yellow oil was dissolved in CH2Cl2/hexane and the solvents were removed under vacuum to give a glassy solid that was crushed into a powder. Two isomers were 20 observed in solution by 1H NMR spectroscopy. These two isomers arise from the coordination of the unsymmetrically substituted ligand in either the cis or trans fashion in regard to the t-butyl groups relative to the square plane of the complex. 25

Example 485

Polymerization of ethylene with [(2-t-BuPh)2DABAn]PdMe(Et₂O)BAF⁻

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A flame-dried 250 mL Schlenk flask was charged with 0.1505 g (1.001x10⁻⁴ mol) of [(2-t-BuPh)₂DABAn]PdMe(Et₂O)BAF in the glove box. The flask was twice evacuated and back-filled with ethylene and then cooled to -60°C. The solid was dissolved in 100 mL of CH₂Cl₂ and the flask was allowed to warm to room temperature with stirring under an atmosphere of ethylene. After stirring for 23 h the polymerization was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in

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petroleum ether and filtered through silica gel. filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless, viscous liquid. Yield = 0.2824 g. 1H NMR analysis: 125 Me/1000 CH₂.

Example 486

A flame-dried 250 mL Schlenk flask was charged with 0.1621 g $(1.003x10^{-4} \text{ mol})$ of [(2,5-t-BuPh) 2DABAn] PdMe (Et20) BAF in the glove box. The flask was twice evacuated and back-filled with ethylene and then cooled to -60°C. The solid was dissolved in 100 mL of CH_2Cl_2 and the flask was allowed to warm to room temperature with stirring under an atmosphere of ethylene. After stirring for 23 h the polymerization was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in petroleum ether and filtered through silica gel. filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless, viscous liquid. Yield = 0.2809 g. ¹H NMR analysis: 20 136 Me/1000 CH₂.

Example 487

A flame-dried 250 mL Schlenk flask was charged with $0.1384 \text{ g} (1.007 \times 10^{-4} \text{ mol})$ of [(2-t-BuPh) 2DABMe2] PdMe (NCMe) BAF in the glove box. flask was twice evacuated and back-filled with ethylene and then cooled to -60°C. The solid was dissolved in 100 mL of CH2Cl2 and the flask was allowed to warm to room temperature with stirring under an atmosphere of After stirring for 23 h the polymerization was quenched with methanol. The solvent was removed under reduced pressure and the polymer was dissolved in petroleum ether and filtered through silica gel. The filtrate was concentrated and the remaining solvent was removed under vacuum to give a clear, colorless, viscous liquid. Yield = 2.40 g. 1 H NMR analysis: Me/1000 CH₂.

Example 488

Under inert conditions, a Schlenk tube was charged with $0.0142 \text{ g} (1.02 \times 10^{-5} \text{ mol})$ of [(2-t-BuPh) 2DABAn] PdMe (Et20) BAF-. The Schlenk tube was cooled to -78°C and the solid was dissolved in 30 mL of CH2Cl2. A 300 mL autoclave was charged with 70 mL of CH2Cl2 under an ethylene atmosphere. The cold catalyst solution was quickly transferred via cannula into the Parr® reactor and the reactor was pressurized to 172 kPa (absolute). The polymerization was stirred for 20 h and the ethylene pressure was released. The red/orange solution was transferred and the solvent was removed under vacuum. A small amount of polyethylene remained after drying under vacuum overnight. Yield = 0.17 g. ¹H NMR analysis: 120 Me/1000 CH₂. 15

Example 489

Following the procedure described in Example 488, 1.68 g of polyethylene was produced using 0.0140 g $(1.02\times10^{-5} \text{ mol})$ of $[(2-t-\text{BuPh})_2\text{DABMe}_2]\text{PdMe}(\text{NCMe})\text{BAF}^-$. Yield = 1.68 g. ¹H NMR analysis: 114 Me/1000 CH₂.

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Example 490

Under nitrogen, Ni(COD)2 (0.017 g, 0.062 mmol) and (2,4,6-MePh) 2DABAn (0.026 g, 0.062 mmol) were dissolved in 2.00 g of cyclopentene to give a purple solution. The solution was then exposed to air for several 25 seconds. The resulting dark red-brown solution was then put back under nitrogen, and EtAlCl2 (1 M solution in toluene, 3.0 mL, 3.0 mmol) was added. A cranberryred solution formed instantly. The reaction mixture was stirred at room temperature for 3 days, during 30 which time polycyclopentene precipitated. The reaction was then quenched by the addition of methanol followed by several drops of concentrated HCl. The reaction mixture was filtered, and the product polymer washed with methanol and dried to afford 0.92 g of 35 polycyclopentene as an off-white powder. Thermal gravimetric analysis of this sample showed a weight loss starting at 141°C: the sample lost 18% of its

weight between 141 and 470°C, and the remaining material decomposed between 470 and 496°C.

Example 491

Under a nitrogen atmosphere, Ni(COD)₂ (0.017 g, 0.06 mmol) and MeC(=N-2,6-C₆H₃-iPr₂)CH=C(NH-C₆H₃-iPr₂)Me (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF $(Et_2O)_2$ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass The glass insert was transferred to a shaker 10 tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C_2H_4 for 40 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of 15 polymer = 1.37 g. Branching per 1000 CH2's was determined by 13 C NMR ($C_6D_3Cl_3$): Total methyls (10.2), Methyl (8.8), Ethyl (1.1), Propyl (0), Butyl (0), ≥Am and end of chains (3.2), ≥Bu and end of chains (.3)

Example 492

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Under a nitrogen atmosphere, Ni(COD)₂ (0.017 g, 0.06 mmol) and the ligand shown below (0.025 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF (Et₂O)₂ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C₂H₄ for 18 h at ambient temperature. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 11.0 g.

Example 493

{[(2.6-i-PrPh)2DABMe2]Pd(n3-CHEtPh)]}BAF

In a nitrogen-filled drybox, 25 mL of Et₂O was added to a flask containing <a>[(2.6-i-PrPh)₂DABMe₂]PdMeCl (402 mg, 0.716 mmol) and NaBAF (633 mg, 0.714 mmol) to yield an orange solution. Styrene (110 μL, 0.960 mmol, 1.35 equiv) was dissolved in ~10 mL of Et₂O and the resulting solution was added to the reaction mixture, which was then stirred for 3 h. Next, the solution was 10 filtered and the solvent was removed in vacuo: resulting orange powder (0.93 g, 87%) was washed with hexane and dried in vacuo. 1H NMR (CD2Cl2, 300 MHz, rt) δ 7.76 (s, 8, BAF: H_0), 7.59 (s, 4, BAF: H_p), 7.46 -7.17 (m, 9, H_{aryl}), 6.29 (d, 1, J = 7.33, H_{aryl}), 5.65 15 $(d, 1, J = 6.59, H_{aryl}), 3.33, 3.13, 2.37 and 1.93$ (septet, 1 each, J = 6.97 - 6.72, $CHMe_2$, $C'HMe_2$, $C''HMe_2$, $C'''HMe_2$), 3.17 (dd, 1, J = 11.36, 3.66, CHEtPh), 2.22 and 2.17 (s, 3 each, N=C(Me)-C'(Me)=N), 20 1.52, 1.45, 1.26, 1.26, 1.19, 1.15, 0.94 and 0.73 (d, 3 each, J = 6.97 - 6.59, CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 0.88 (t, 3, J = 0.88, $CH(CH_2CH_3)Ph$), 1.13 and -0.06 (m, 1 each, $CH(CHH'CH_3)Ph$); ^{13}C NMR (CD_2Cl_2 , 75 MHz, rt) δ 176.6 and 174.0 (N=C-C'=N), 162.2 (q, J_{CB} = 49.3, BAF: Cipso), 142.8 and 142.4 (Ar, Ar': Cipso), 25 138.2, 137.3, 137.1, and 136.9 (Ar, Ar': C_o), 135.2 (BAF: C_0, C_0), 134.6 and 132.2 (Ph: $C_0, C_m, \text{ or } C_p$)), 129.4 (BAF: C_m), 129.0 and 128.5 (Ar, Ar': C_p), 125.1, 125.1, 124.9 and 124.7 (Ar, Ar': C_m), 125.1 (q, J_{CF} = 30 272.5, BAF: CF₃), 120.2 (Ph: C_{ipso}) and 120.0 (Ph: C_o, C_m , or C_p), 117.9 (BAF: C_p), 103.0 and 88.6 (Ph: C_o ' and C_m'), 69.1(CHEtPh), 29.9, 29.7, 29.12 and 29.09 (CHMe2, C'HMe2, C''HMe2, C'''HMe2), 24.4, 24.3, 23.5, 23.4, 23.1, 23.0, 22.9, and 22.7 (CHMeMe', C'HMeMe', C''HMeMe', C'''HMeMe'), 20.8, 20.65, and 20.61 35

 $(N=C(Me)-C'(Me)=N, CH(CH_2CH_3)Ph)), 13.1 (CH(CH_2CH_3)Ph).$

Example 494

 $\{[(2,6-i-PrPh)_2DABH_2]Pd(n^3-CHEt(4-C_6H_4-t-Bu)]\}BAF$ t-Butylstyrene (230 μL, 1.26 mmol, 1.10 equiv) was added via microliter syringe to a mixture of [(2.6-i-PrPh) 2DABH2 PdMeCl (611 mg, 1.15 mmol) and NaBAF (1.01 g, 1.14 mmol) dissolved in 25 mL of Et_2O . additional 25 mL of Et₂O was added to the reaction mixture, which was then stirred for ~12 h. resulting deep red solution was filtered, and the solvent was removed in vacuo to yield a sticky red 10 solid. The solid was washed with 150 mL of hexane and the product was dried in vacuo. A dull orange powder (1.59 g, 91.7%) was obtained: ^{1}H NMR (CD₂Cl₂, 400 MHz, rt) δ 8.34 and 8.16 (s, 1 each, N=C(H)-C'(H)=N), 7.72 (s, 8, BAF: H_o), 7.56 (s, 4, BAF: H_p), 7.5 - 7.1 (m, 8, 15 H_{aryl}), 6.88 (dd, 1, J = 7.1, 1.9, H_{aryl}), 6.11 (dd, 1, J = 7.3, 2.0, H_{aryl}), 3.49, 3.37, 2.64 and 2.44 (septet, 1 each, J = 6.6 - 6.9, $CHMe_2$, $C'HMe_2$, $C''HMe_2$ and $C'''HMe_2$), 3.24 (dd, 1, J = 11.3, 4.1, $CHEt(4-C_6H_4-t-$ Bu)), 1.52, 1.48, 1.24, 1.24, 1.19, 1.18, 1.0 and 0.70 20 (d, 3 each, J = 6.8 - 6.9, CHMeMe', C'HMeMe', C''HMeMe', and C'''HMeMe'), 1.42 and 0.25 (m, 1 each, $CH(CHH'CH_3)(4-C_6H_4-t-Bu)), 0.98 (s, 9, t-Bu), 0.87 (t,$ 3, J = 7.4, $CH(CH_2CH_3)(4-C_6H_4-t-Bu)$; ¹³C NMR (CD_2Cl_2 , 100 MHz, rt) δ 165.0 (J_{CH} = 165, N=C(H)), 163.3 (J_{CH} = 165, N=C'(H)), 162.2 (q, $J_{CB} = 49.9$, BAF: C_{ipso}), 157.0 $(C_6H_4-t-Bu: C_p)$, 144.9 and 144.6 (Ar, Ar': C_{ipso}), 139.0, 138.4, 138.2 and 137.4 (Ar, Ar': Co, Co'), 135.2 (BAF: C_o), 133.3, 129.8, 129.6 and 129.2 (Ar, Ar': C_p; $C_6H_4-t-Bu: C_0, C_m)$, 129.3 (q, BAF: C_m), 125.0 (q, $J_{CF} =$ 30 272, BAF: CF₃), 124.7, 124.64, 124.55, and 124.3 (Ar, Ar': C_m , C_m '), 117.9 (BAF: C_p), 119.1, 116.4 and 94.9 $(C_6H_4-t-Bu: C_m', C_{ipso}, C_o'), 68.5 (CHEt), 36.2 (CMe_3),$ $30.2 \text{ (CMe}_3)$, 30.1, 29.9, 28.80 and 28.77 (CHMe_2 , C'HMe2, C''HMe2 and C'''HMe2), 25.0, 24.8, 24.1, 22.8, 35 22.7, 22.45, 22.36, and 22.1 (CHMeMe', C'HMeMe', C''HMeMe' and C'''HMeMe'), 21.7 $(CH(CH_2CH_3))$, 13.2 (CH(CH₂CH₃)). Anal. Calcd for (C₇₁H₆₇BF₂₄N₂Pd): C, 401

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56.05; H, 4.44; N, 1.84. Found: C, 56.24; H, 4.22; N, 1.59.

Example 495

Example 496

 $\{[(2.6-i-PrPh)_2DABH_2]Ni[\eta^3-CHEt(4-C_6H_4-t-Bu)]\}BAF$ In the drybox, {[(2.6-i-PrPh)2DABMe2]NiMe(OEt2)}BAF (22.4 mg, 0.0161 mmol) was placed in an NMR tube. 15 tube was sealed with a septum and Parafilm®, removed from the drybox, and cooled to -78° C. CD_2Cl_2 (700 μ L) and $H_2C=CH(4-C_6H_4-t-Bu)$ (15 μ L, 5.10 equiv) were then added via gastight microliter syringe to the cold tube in sequential additions. The septum was sealed with a 20 small amount of grease and more Parafilm, the tube was shaken briefly and then transferred to the cold (-78°C) NMR probe. Insertion of t-butylstyrene was observed at -78°C and was complete upon warming to -50°C to yield the π -benzyl complex: ¹H NMR (CD₂Cl₂, 400 MHz, -50;C) δ 25 8.43 and 8.18 (s, 1 each, N=C(H)-C'(H)=N), 7.76 (s, 8, BAF: H_0), 7.58 (s, 4, BAF: H_p), 7.5 - 7.1 (m, 8, H_{aryl}), 6.80 (d, 1, J = 7.3, H_{aryl}), 6.15 (d, 1, J = 7.7, H_{arvl}), 3.72, 3.18, 2.68 and 2.50 (septet, 1 each, J =6.5 - 6.7, CHMe₂, C'HMe₂, C''HMe₂ and C'''HMe₂), 2.56 30 (dd, 1, J = 11.5, 3.9, CHEt), 1.6 - 0.8 (CHMeMe',C'HMeMe', C''HMeMe', C'''HMeMe', and CH(CHH'CH3)), 0.94 $(s, 9, CMe_3), 0.72 (t, 3, J = 7.3, CH(CH_2CH_3)), -0.04$ (m, 1, CH(CHH'CH₃)).

Examples 497-515

General Procedure for the Synthesis of π -Allyl Type Nickel Compounds

A mixture of one equiv. of the appropriate α diimine, one equiv of NaBAF, and 0.5 equiv of [(allyl)Ni(μ -X)]₂ (X = Cl or Br) was dissolved in Et₂O. The reaction mixture was stirred for ~2 h before being filtered. The solvent was removed in vacuo to yield the desired product, generally as a red or purple powder. (The [(allyl)Ni(μ -X)]₂ precursors were 10 synthesized according to the procedures published in the following reference: Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. Angew. Chem. Int. Ed. Engl. 1966, 5, 15 151-164.) The following compounds were synthesized according to the above general procedure.

Example 497

 $\{ [(2,4,6-MePh)_2DABMe_2] Ni(\eta^3-C_3H_5) \} BAF$ Example 498 20 $\{[(2,6-i-PrPh)_2DABMe_2]Ni(\eta^3-C_3H_5)\}BAF$ Example 499 $\{[(2.6-i-PrPh)_2DABMe_2]Ni(\eta^3-H_2CCHCHMe)\}BAF$ Example 500 $\{[(2,6-i-PrPh)_2DABMe_2]Ni(\eta^3-H_2CCHCHPh)\}BAF$ 25 Example 501 $\{[(2.6-i-PrPh)_2DABMe_2]Ni(\eta^3-H_2CCHCMe_2)\}BAF$ Example 502 $\{[(2.6-i-PrPh)_2DABAn]Ni(\eta^3-C_3H_5)\}BAF$ Example 503 30 $\{ (2,6-i-PrPh)_2DABAn \}$ Ni $(\eta^3-H_2CCHCHMe) \}$ BAF

> Example 504 $\{[(2,6-i-PrPh)_2DABAn]Ni(\eta^3-H_2CCHCHPh)\}BAF$ Example 505

 $\{[(2,6-i-PrPh)_2DABAn]Ni(\eta^3-H_2CCHCMe_2)\}BAF$ 35 Example 506

 $\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CCHCHMe)\}BAF$

	Example 507
	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CCHCHPh)\}BAF$
	Example 508
	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-C_3H_5)\}BAF$
5 >	Example 509
	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CCHCMe_2)\}BAF$
	Example 510
	$\{ [(2,6-i-PrPh)_2DABAn] Ni (\eta^3-H_2CC(COOMe) CH_2) \} BAF$
. •	Example 511
10	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CC(COOMe)CH_2)\}BAF$
	Example 512
	$\{[(2.6-i-PrPh)_2DABAn]$ Ni $(\eta^3-H_2CCHCH(COOEt)]$ BAF
	Example 513
	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CCHCH(COOEt)\}BAF\}$
15	Example 514
	$\{[(2,6-i-PrPh)_2DABAn]$ Ni $(\eta^3-H_2CCHCHCl)\}$ BAF
	Example 515
	$\{[(2,4,6-MePh)_2DABAn]Ni(\eta^3-H_2CCHCHCl)\}BAF$
	Examples 516-537
20	Polymerizations catalyzed by nickel and palladi
	π -benzyl initiators and by nickel allyl initiators a
	133

Polymerizations catalyzed by nickel and palladium π -benzyl initiators and by nickel allyl initiators are illustrated in the following Table containing Examples 516-537. The initiation of polymerizations catalyzed by nickel allyl initiators where the allyl ligand was substituted with functional groups, such as chloro or ester groups, was often aided by the addition of a Lewis acid.

Example	Compound	Conditions	Results
	$\{[(2,6-i-PrPh)_2DABMe_2]Pd(\eta^3-$	0.067 mmol Cmpd; 25 °C; 1	<0.5 g PE
516	CHEtPh)}BAF	atm E; 2 days; CH ₂ Cl ₂	(270 TO)
	and a property of the second o	0.027 mmol Cmpd; 25 °C;	8.2 g PE
	{[(2,6-i-PrPh) ₂ DABMe ₂]Pd(η ³ -	6.9 MPa E; 18 h; C ₆ D ₆	(11,000
517	CHEtPh)}BAF	0.5 Mil a 2, 10 ii, 0020	TO)
	·		
•	$\{[(2,6-i-PrPh)_2DABH_2]Pd(\eta^3-CHEt(4-i)\}$	0.016 mmol Cmpd; 25 °C;	1.5 g PE
518	C6H4-1-Bu))}BAF	6.9 MPa E; 18 h; C6D6	(3,300 TO)
•	3 DADIS 104/-3	0.063 mmol Cmpd; 25 °C; 1	4.6 g PE
•	{{(2,6-i-PrPh) ₂ DABMe ₂]Pd(η ³ -	atm E; 5 days; CH ₂ Cl ₂	(2,600 TO)
519	CHEtC ₆ F ₅)}BAF	aun E, 5 days, C112C12	(2,000 10)
	{[(2,6-i-PrPh) ₂ DABMe ₂]Pd(η ³ -	0.044 mmol Cmpd; 25 °C;	6.4 g PE
520	CHEtC6F5)}BAF	6.9 MPa E; 18 h; C6D6	(5,200 TO)
			1.6 - DC
	{[(2,4,6-MePh) ₂ DABAn]Ni(η ³ -	0.049 mmol Cmpd; 25 °C;	1.5 g PE
521	H ₂ CCHCMe ₂)}BAF	6.9 MPa E; 18 h; C ₆ D ₆	(1,100 TO)
	{[(2,6-i-PτPh) ₂ DABMe ₂]Ni(η ³ -	0.034 mmol Cmpd; 25 °C;	35 mg PE
522	H ₂ CCHCMe ₂)}BAF	6.9 MPa E; 18 h; C ₆ D ₆	(37 TO)
			·
•	{[(2,4,6-MePh) ₂ DABMe ₂]Ni(η ³ -	0.047 mmol Cmpd; 80 °C;	20 mg PE
523	C ₃ H ₅)}BAF	6.9 MPa E; 18 h; C ₆ D ₆	(15 TO)
	{[(2,4,6-MePh) ₂ DABAn]Ni(η ³ -	0.034 mmol Cmpd; 80 °C;	260 mg PE
524	(((2,4,5)))BAF	6.9 MPa E; 18 h; C ₆ D ₆	(270 TO)
327	-33//		
	{[(2,4,6-MePh) ₂ DABAn]Ni(η ³ -	0.026 mmol Cmpd; 80 °C;	141 mg PE
525	H ₂ CCHCHPh)}BAF	6.9 MPa E; 18 h; C ₆ D ₆	(190 TO)
			
	(((a c : p-ph)-p-a p-a-lhii/n-3	0.040 mmol Cmpd; 80 °C;	992 mg PE
	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ -	6.9 MPa E; 18 h; C ₆ D ₆	(880 TO)
526	H ₂ CCHCHPh)}BAF	10.7 111 11 2, 10 11, 0020	,

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527	{[(2,6-i-PτPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHMe)}BAF	0.043 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; C ₆ D ₆	23 mg PE (19 TO)
528	{[(2,6-i-PrPh) ₂ DABMe ₂]Ni(η ³ - H ₂ CCHCMe ₂)}BAF	0.044 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; C ₆ D ₆	54 mg PE (44 TO)
529	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - C ₃ H ₅)}BAF	0.042 mmol Cmpd; 80 °C; 6.9 MPa E; 18 h; C ₆ D ₆	15 mg PE (13 TO)
530	{[(2,4,6-MePh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.043 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; C ₆ D ₆	94 mg PE (78 TO)
531	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.042 mmol Cmpd; 25 °C; 6.9 MPa E; 18 h; C ₆ D ₆	8 mg PE (7 TO)
532	{[(2,4,6-MePh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.020 mmol Cmpd; 0.04 mmol B(C ₆ F ₅) ₃ ; 25 °C; 6.9 MPa E; 18 h; CDCl ₃	7.8 g PE (14,000 TO)
533	{[(2,4,6-MePh) ₂ DABAπ]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.020 mmol Cmpd; 0.04 mmol BPh3; 25 °C; 6.9 MPa E; 18 h; CDCl3	8.4 g PE (15,000 TO)
534	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCH(COOEt))}BAF	0.020 mmol Cmpd; 0.04 mmol BPh3; 25 °C; 6.9 MPa E; 18 h; CDCl3	4.7 g PE (8,400 TO)
535	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.020 mmol Cmpd; 0.04 mmol BPh3; 80 °C; 6.9 MPa E; 18 h; C6D6	6.8 g PE (12,000 TO)
536	{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCHCl)}BAF	0.020 mmol Cmpd; 10 mg montmorillonite; 80 °C; 6.9 MPa E; 18 h; C ₆ D ₆	326 mg PE (580 TO)

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{[(2,6-i-PrPh) ₂ DABAn]Ni(η ³ - H ₂ CCHCH(COOEt)}BAF 0.020 mmol Cmpd; 0.04 10.3 g P mmol BPh3; 80 °C; (18,000	0.020 mmol Cmpd; 0.04 10.3 g PE mmol BPh3; 80 °C; (18,000
6.9 MPa E; 18 h; C ₆ D ₆ TO)	

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What is claimed is:

- 1. A polyolefin, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.
- 2. The polyolefin as recited in claim 1 which contains about 100 to about 130 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 50 to about 75 ethyl branches, about 5 to about 15 propyl branches, about 24 to about 40 butyl branches, about 5 to about 10 amyl branches, and about 65 to about 120 hexyl or longer branches.
 - 3. The polyolefin as recited in claim 1 which is an ethylene homopolymer.
- 4. A polyolefin which contains about 20 to about

 150 branches per 1000 methylene groups, and which
 contains for every 100 branches that are methyl, about
 4 to about 20 ethyl branches, about 1 to about 12
 propyl branches, about 1 to about 12 butyl branches,
 about 1 to about 10 amyl branches, and 0 to about 20

 25 hexyl or longer branches.
 - 5. The polyolefin as recited in claim 4 which contains about 40 to about 100 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 6 to about 15 ethyl branches, about 2 to about 10 propyl branches, about 2 to about 10 butyl branches, about 2 to about 8 amyl branches, and about 2 to about 15 hexyl or longer branches.
 - 6. The polyolefin as recited in claim 4 which is an ethylene homopolymer.
 - 7. A polymer, consisting essentially of units derived from the monomers ethylene and a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen,

hydrocarbyl or substituted hydrocarbyl, and m is 0 or an integer from 1 to 16, and which contains about 0.01 to about 40 mole percent of repeat units derived from said compound, and provided that said repeat units derived from said compound are in branches of the formula $-CH(CH_2)_nCO_2R^1$, in about 30 to about 70 mole percent of said branches n is 5 or more, in about 0 to about 20 mole percent n is 4, in about 3 to 60 mole percent n is 1, 2 and 3, and in about 1 to about 60 mole percent n is 0.

- 8. The polymer as recited in claim 7 wherein m is 0.
- 9. The polymer as recited in claim 7 wherein R^1 is hydrocarbyl or substituted hydrocarbyl.
- 15 10. The polymer as recited in claim 7 wherein R¹ is alkyl containing 1 to 10 carbon atoms.
 - 11. The polymer as recited in claim 8 wherein R¹ is hydrocarbyl or substituted hydrocarbyl.
 - 12. The polymer as recited in claim 7 wherein about 0.1 to about 20 mole percent of said units are derived from said compound.
 - 13. A process for the polymerization of olefins, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of

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(XXIII)

(XXXII)

5 with an olefin wherein:

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said olefin is selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, norbornene, or a substituted norbornene,;

said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd;

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

 R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring; each R^{30} is independently hydrogen, substituted

5 hydrocarbyl or hydrocarbyl, or two of R³⁰ taken together form a ring;

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 ${\ensuremath{\mathbb{R}}}^{21}$ and ${\ensuremath{\mathbb{R}}}^{22}$ are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R¹ is hydrogen, hydrocarbyl or substituted
hydrocarbyl;

n is 2 or 3;

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and provided that:

when said bidentate ligand is (XXX) M is not Pd;

when M is Pd a diene is not present; and said transition metal also has bonded to it a ligand that may be displaced by said olefin or add to said olefin;

when norbornene or substituted norbornene is used no other olefin is present.

- 14. The process as recited in claim 13 wherein said transition metal is Co, Fe, Ni or Pd.
- 30 15. The process as recited in claim 13 wherein said transition metal is Ni or Pd.
 - 16. The process as recited in claim 13 or 15 wherein said olefin is ethylene, $R^{17}CH=CH_2$, or cyclopentene , wherein R^{17} is n-alkyl.
- 35 17. The process as recited in claim 13 wherein said olefin comprises cyclopentene.
 - 18. The process as recited in claim 13, 14, 15, or 16 wherein said bidentate ligand is (VIII).

19. The process as recited in claim 18 wherein said olefin is ethylene.

- 20. The process as recited is in claim 18 wherein said olefin is propylene.
- 21. The process as recited in claim 18 wherein said olefin is a combination of ethylene and propylene.
- 22. The process as recited in claim 18 wherein said olefin is contained in a mixed butenes stream.
- 23. The process as recited in claim 18 wherein R² and R⁵ are each independently hydrocarbyl provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a carbocyclic ring.
- 15 24. The process as recited in claim 18 wherein R³ and R⁴ are each independently hydrogen or methyl or together are 1,8-naphthylylene, and both R² and R⁵ are 2,6-diisopropylphenyl.
- 25. The process as recited in claim 18 wherein20 said olefin comprises cyclopentene.
 - 26. A process for the copolymerization of an olefin and a fluorinated olefin, comprising, contacting a transition metal complex of a bidentate ligand selected from the group consisting of

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with an olefin, and a fluorinated olefin wherein:

said olefin is selected from the group consisting of ethylene and an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$;

said transition metal is selected from the group consisting of Ni and Pd;

said fluorinated olefin is of the Formula $H_2C=CH\left(CH_2\right){}_aR_fR^{42}$;

a is an integer of 2 to 20; R_f is perfluoroalkylene optionally containing one or more ether groups;

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R42 is fluorine or a functional group;

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R^{17} is independently saturated hydrocarbyl;

and provided that said transition metal also has bonded to it a ligand that may be displaced by said olefin or added to said olefin.

- 27. The process as recited in claim 26 wherein R⁴² is fluorine, ester or sulfonyl halide.
 - 28. The process as recited in claim 26 wherein R_f is $-(CF_2)_b-$, wherein b is 2 to 20, or $-(CF_2)_dOCF_2CF_2-$ wherein d is 2 to 20.
 - 29. The process as recited in claim 26 or 27 wherein said olefin is ethylene or wherein said olefin is $R^{17}CH=CH_2$, wherein R^{17} is n-alkyl.
 - 30. The process as recited in claim 26 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.
- 31. A copolymer of an olefin of the formula $R^{17}CH=CHR^{17}$ and a fluorinated olefin of the formula $H_2C=CH(CH_2)_aR_fR^{42}$, wherein:

each R^{17} is independently hydrogen or saturated hydrocarbyl;

a is an integer of 2 to 20; $R_{\rm f}$ is perfluoroalkylene optionally containing one or more ether groups; and

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 R^{42} is fluorine or a functional group; provided that when both of R^{17} are hydrogen and R^{42} is fluorine, R_f is $-(CF_2)_b$ - wherein b is 2 to 20 or perfluoroalkylene containing at least one ether group.

- 10 32. The copolymer as recited in claim 31 wherein \mathbb{R}^{42} is fluorine, ester, sulfonic acid, or sulfonyl halide.
 - 33. The copolymer as recited in claim 31 wherein R_f is $-(CF_2)_b$ -, wherein b is 2 to 20, or $-(CF_2)_dOCF_2CF_2$ -wherein d is 2 to 20.
 - 34. The copolymer as recited in claim 31 or 32 wherein said olefin is ethylene or wherein said olefin is $R^{17}CH=CH_2$, wherein R^{17} is n-alkyl.
- 35. The copolymer as recited in claim 31 wherein 20 said fluorinated olefin is about 1 to 20 mole percent of repeat units in said copolymer.
 - 36. An acid catalyst of the composition of claim 31, wherein \mathbb{R}^{42} is sulfonic acid.
- 37. A process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

$$\begin{array}{c|c}
R^{2} \\
N \\
N \\
(S)_{z} \\
R^{5}
\end{array}$$
(XI)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd in the m oxidation state;

y + z = m

 ${\ R}^2$ and ${\ R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or

25 bromide;

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S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is 30 present, no other monomer is present;

when M is Pd a diene is not present; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 38. The process as recited in claim 37 wherein said monomer is ethylene only.
- 39. The process as recited in claim 37 wherein said monomer is an $\alpha\text{-olefin}$ only.
- 40. The process as recited in claim 39 wherein said $\alpha\text{-olefin}$ is propylene.
- 10 41. The process as recited in claim 37 done in the presence of a solvent.
 - 42. The process as recited in claim 41 wherein R^3 and R^4 are each independently hydrogen or methyl, or R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.
 - 43. The process as recited in claim 37 used to make a block polymer.

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- 44. The process as recited in claim 37 wherein: M is Ti(IV), Q and S are chloride, and y and z are
- - M is Co(II), Q and S are bromide, and y and z are 1;
- M is Fe(II), Q and S are chloride, and y and z are 1;
 - M is Sc(III), Q and S are chloride, y is 1 and z is 2;
- \$M\$ is Ni(II), Q and S are bromide or chloride, and 30 $\,$ y and z are 1;
 - M is Pd(II), Q and S are methyl, and y and z are 1;
 - M is Pd(II), Q and S are chloride, and y and z are 1;
- M is Ni(I), Q is methyl, chloride, bromide, iodide or acetylacetonate, y is 1, and z is 0;
 - M is Pd(II), Q is methyl and S is chloride, and y and z are 1; or

M is Ni(II), Q and S are methyl, and y and z are 1.

- 45. The process as recited in claim 37 wherein ethylene and propylene are the monomers.
- 46. The process as recited in claim 37 wherein said monomers are part of a crude butenes stream.

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- 47. The process as recited in claim 37 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.
- 48. The process as recited in claim 37 wherein said monomer comprises cyclopentene.
- 49. A process for the production of polyolefins, comprising, contacting, at a temperature of about 100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹¹CH=CH2 or R¹¹CH=CHR¹¹, cyclobutene, cyclopentene, substituted norbornene, and norbornene; and a compound of the formula

or

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wherein:

 $\rm R^2$ and $\rm R^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion;

 ${\ensuremath{\mathsf{R}}}^{15}$ is hydrocarbyl not containing olefinic or acetylenic bonds;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

each R^{16} is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

R^B is hydrocarbyl; and

T² is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted

with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

provided that:

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when M is Pd, or (II) or (VII) are present, a diene is not present; and

when norbornene or substituted norbornene is used no other monomer is present.

- 50. The process as recited in claim 49 wherein said monomer is ethylene only.
- 10 51. The process as recited in claim 49 wherein said monomer is an α -olefin only.
 - 52. The process as recited in claim 51 wherein said α -olefin is propylene.
- 53. The process as recited in claim 49 wherein said compound is (II), (IV) or (VII), M is Pd(II), and a comonomer selected from the group consisting of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone, is also present.
 - 54. The process as recited in claim 53 wherein m is 0, and R^1 is hydrocarbyl or substituted hydrocarbyl.
- 55. The process as recited in claim 49 done in the 25 presence of a solvent.
 - 56. The process as recited in claim 49 done in the absence of a solvent.
 - 57. The process as recited in claim 49 wherein R^3 and R^4 are each independently hydrogen or methyl, or R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.
 - 58. The process as recited in claim 49 used to make a block polymer.
- 59. The process as recited in claim 49 wherein X is BAF, SbF₆, PF₆, or BF₄.
 - 60. The process as recited in claim 57 wherein X is BAF, SbF_6 , PF_6 , or BF_4 .

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61. The process as recited in claim 60 wherein a monomer is ethylene or propylene.

- 62. The process as recited in claim 49 wherein the monomers are ethylene and propylene.
- 63. The process as recited in claim 49 wherein said monomers are part of a crude butenes stream.
- 64. The process as recited in claim 49 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a carbocyclic ring.
- 65. A process for the production of polyolefins,

 comprising contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹7CH=CH2 or R¹7CH=CHR¹7, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

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R²⁸
$$(CR^{30}_2)_n$$
 R²⁹ $(CR^{30}_2)_n$ R²⁹ $(CR^{30}_2)_n$ R²⁹ $(CR^{45}_3)_n$ $(CR^{20}_4)_n$ $(CR^$

wherein:

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

 ${\ R}^{45}$ is hydrocarbyl or substituted hydrocarbyl, and ${\ R}^{29}$ is hydrogen, substituted hydrocarbyl or

hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl or two of R^{30} taken together form a ring; R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 ${\mbox{R}}^{21}$ and ${\mbox{R}}^{22}$ are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

n is 2 or 3;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

M is Ti, Zr, Sc, Cr, a rare earth metal, V, Fe, Co, Ni or Pd the m oxidation state;

for (XVII),
$$y + z = m$$
;

for (XIII), m is 2;

Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or

5 bromide;

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 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6; and

X is a weakly coordinating anion; and provided that:

when said compound is (XVII) M is not Pd; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 66. The process as recited in claim 65 wherein said monomer is ethylene only.
- 67. The process as recited in claim 65 wherein said monomer is an α -olefin only.
- 25 68. The process as recited in claim 67 wherein said α -olefin is propylene.
 - 69. The process as recited in claim 66 wherein M is Pd(II) and one or more comonomer is selected from the group consisting of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.
 - 70. The process as recited in claim 69 wherein m is 0, and \mathbb{R}^1 is hydrocarbyl or substituted hydrocarbyl.
 - 71. The process as recited in claim 65 done in the presence of a solvent.

72. The process as recited in claim 65 done in the absence of a solvent.

73. The process as recited in claim 65 used to make a block polymer.

74. The process as recited in claim 65 wherein X is BAF, SbF₆, PF₆, or BF₄.

75. The process as recited in claim 74 wherein a monomer is ethylene or propylene.

76. The process as recited in claim 75 wherein the monomers are ethylene and propylene.

77. The process as recited in claim 65 wherein said monomers are part of a crude butenes stream.

78. The process as recited in claim 65 wherein: R^{44} is hydrocarbyl, and R^{28} is hydrogen or

hydrocarbyl, or R⁴⁴ and R²⁸ taken together form a ring;

R⁴⁵ is hydrocarbyl, and R²⁹ is hydrogen or

hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring;

hydrocarbyl, or R^{45} and R^{29} taken together form a ring; each R^{30} is independently hydrogen or

hydrocarbyl, or two of R^{30} taken together form a ring; R^{21} and R^{22} are each in independently hydrogen or hydrocarbyl; and

 R^{20} and R^{23} are independently hydrocarbyl.

79. A process for the production of polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene; with a compound of the formula

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$$\begin{array}{c|c}
R^{20} \\
H \\
R^{21} \\
N \\
T^{2} \\
R^{22} \\
N \\
X \\
R^{23}
\end{array}$$

(XVIII)

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wherein:

 $$\rm R^{20}$$ and $\rm R^{23}$ are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

X is a weakly coordinating anion;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic

bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

M is Ni(II) or Pd(II);

 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

and provided that:

when M is Pd a diene is not present; and when norbornene or substituted norbornene is used no other monomer is present.

- 80. The process as recited in claim 79 wherein said monomer is ethylene only.
- 81. The process as recited in claim 79 wherein said monomer is an $\alpha\text{-olefin}$ only.
- 25 82. The process as recited in claim 81 wherein said α -olefin is propylene.
 - 83. The process as recited in claim 79 wherein T^2 is methyl; R^{20} and R^{23} are independently hydrocarbyl; and R^{21} and R^{22} are each in independently hydrogen or hydrocarbyl.
 - 84. A process for the production for polyolefins, comprising contacting, at a temperature of about -100°C to about +200°C,
- a first compound W, which is a neutral Lewis

 35 acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

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a second compound of the formula

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ti, Zr, V, Cr, a rare earth metal, Co, Fe, Sc, or Ni, of oxidation state m;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{44} and R^{28} taken together form a ring;

 R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken

20 together form a ring;

n is 2 or 3;

y and z are positive integers;

y+z = m;

each R¹⁷ is independently hydrocarbyl or

25 substituted hydrocarbyl provided that any olefinic bond
in said olefin is separated from any other olefinic
bond or aromatic ring by a quaternary carbon atom or at
least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or

30 bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that;

when norbornene or substituted norbornene is present, no other monomer is present.

- 85. The process as recited in claim 84 wherein R^{28} , R^{29} , and each of R^{30} are hydrogen.
 - 86. The process as recited in claim 84 wherein said monomer is ethylene only.
 - 87. The process as recited in claim 84 wherein said monomer is an $\alpha\text{-olefin}$ only.
- 10 88. The process as recited in claim 87 wherein said α -olefin is propylene.
 - 89. The process as recited in claim 84 done in the presence of a solvent.
- 90. The process as recited in claim 84 wherein both R^{44} and R^{45} are 2,4,6-trimethylphenyl.
 - 91. The process as recited in claim 84 used to make a block polymer.
 - 92. The process as recited in claim 90 wherein a monomer is ethylene or propylene.
- 20 93. The process as recited in claim 84 wherein: M is Ti(IV), Q and S are chloride, and y and z are 2;
 - M is Zr(IV), Q and S are chloride, and y and z are 2;
- M is Co(II), Q and S are bromide, and y and z are 1;
 - M is Fe(II), Q and S are chloride, and y and z are 1;
- M is Sc(III), Q and S are chloride, y is 1 and z 30 is 2;
 - M is Ni(II), Q and S are bromide or chloride, and
 y and z are 1;
 - M is Pd(II), Q and S are chloride, and y and z are 1;
- M is Pd(II), Q and S are methyl, and y and z are 1:
 - M is Ni(I), Q is methyl, chloride, bromide, iodide or acetylacetonate, y is 1, and z is 0;

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M is Pd(II), Q is methyl and S is chloride, and y and z are 1; or

M is Ni(II), Q and S are methyl, and y and z are 1.

- 94. The process as recited in claim 84 wherein ethylene and propylene are the monomers.
- 95. The process as recited in claim 84 wherein said monomers are part of a crude butenes stream.
 - 96. The process as recited in claim 84 wherein:

10 R⁴⁴ is hydrocarbyl, and R²⁸ is hydrogen or hydrocarbyl, or R⁴⁴ and R²⁸ taken together form a ring; R⁴⁵ is hydrocarbyl, and R²⁹ is hydrogen or hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring; and

each R^{30} is independently hydrogen or hydrocarbyl, or two of R^{30} taken together form a ring.

97. A process for the production of polyolefins, comprising, contacting, at a temperature of about - 100°C to about +200°C, one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, and norbornene; optionally a source of X⁻, and a compound of the formula

$$\begin{array}{c|ccccc}
R^3 & R^2 & R^2 & R^3 \\
\hline
R^4 & N & R^5 & R^5 & R^4 \\
\hline
R^5 & R^5 & R^5 & X
\end{array}$$
(V)

wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4

taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} contains no olefinic bonds;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -; R^{15} is hydrocarbyl not containing olefinic or acetylenic bonds;

E is halogen or -OR¹⁸;

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 $\ensuremath{\text{R}^{18}}$ is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion;

provided that when norbornene or substituted norbornene is present no other monomer is present.

- 98. The process as recited in claim 97 wherein said monomer is ethylene only.
- 99. The process as recited in claim 97 wherein said monomer is an $\alpha\text{-olefin}$ only.
- 20 100. The process as recited in claim 99 wherein said α -olefin is propylene.
 - 101. The process as recited in claim 97 wherein E is chlorine.
- 102. The process as recited in claim 97 wherein T^1 is alkyl.
 - 103. The process as recited in claim 97 done in the presence of a solvent.
 - 104. The process as recited in claim 98 wherein E is chlorine and $\textbf{T}^{\textbf{l}}$ is alkyl.
- 30 105. The process as recited in claim 104 wherein R^3 and R^4 are each independently hydrogen or methyl or R^3 and R^4 taken together are 1,8-naphthylylene, both R^2 and R^5 are 2,6-diisopropylphenyl, and T^1 is methyl.
- 106. The process as recited in claim 97 used to 35 make a block polymer.
 - 107. The process as recited in claim 105 wherein X is BAF, SbF₆, PF₆, or BF₄.

108. The process as recited in claim 107 wherein a monomer is ethylene or propylene.

- 109. The process as recited in claim 97 wherein the monomers are ethylene and propylene.
- 110. The process as recited in claim 97 wherein said monomers are part of a crude butenes stream.
- and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring.
- 112. A process for the polymerization of olefins, comprising, contacting, at a temperature of about 100°C to about +200°C:
- a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; a second compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, 4-vinylcyclohexene, cyclobutene, cyclopentene, substituted norbornene, and norbornene;

wherein:

M is Ni(II), Co(II), Fe(II) or Pd(II);

 $\rm R^2$ and $\rm R^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${
m R}^3$ and ${
m R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or ${
m R}^3$ and ${
m R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide, or bromide; and

provided that:

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when norbornene or substituted norbornene is present, no other monomer is present, and further provided that when 4-vinylcyclohexene is present M is Ni;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 113. The process as recited in claim 112 wherein said monomer is ethylene only.
- 30 114. The process as recited in claim 112 wherein said monomer is an α -olefin only.
 - 115. The process as recited in claim 114 wherein said $\alpha\text{-olefin}$ is propylene.
- 116. The process as recited in claim 112 done in the presence of a solvent.
 - 117. The process as recited in claim 112 wherein \mathbb{R}^3 and \mathbb{R}^4 are each independently hydrogen or methyl or

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both of R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.

- 118. The process as recited in claim 112 used to make a block polymer.
- 119. The process as recited in claim 112 wherein a monomer is ethylene or propylene.
- 120. The process as recited in claim 112 wherein the molar ratio of said first compound: said second compound (I) is about 5 to about 1000.
- 121. The process as recited in claim 112 wherein the molar ratio of said first compound: said second compound (I) is about 10 to about 100.
- 122. The process as recited in claim 112 wherein said first compound is R⁹AlCl₂, R⁹₂AlCl, R⁹₃Al₂Cl₃, or an alkylaluminoxane in which the alkyl group has 1 to 4 carbon atoms, and wherein R⁹ is alkyl containing 1 to 4 carbon atoms.
- 123. The process as recited in claim 120 wherein said first compound is R⁹AlCl₂, R⁹₂AlCl, R⁹₃Al₂Cl₃, or an alkylaluminoxane in which the alkyl group has 1 to 4 carbon atoms, and wherein R⁹ is alkyl containing 1 to 4 carbon atoms.
- 124. The process as recited in claim 112 wherein the monomer comprises cyclopentene.
- 25 125. The process as recited in claim 112 wherein said monomers are part of a crude butenes stream.
 - 126. The process as recited in claim 112 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.
 - 127. A polymerization process, comprising, contacting a compound of the formula $[Pd(R^{13}CN)_4]X_2$, or a combination of $Pd[OC(O)R^{40}]_2$ and HX, with a compound of the formula

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(VIII)

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene, wherein:

 $\rm R^2$ and $\rm R^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl providedR¹⁷ contains no olefinic bonds;

R¹³ is hydrocarbyl;

 R^{40} is hydrocarbyl or substituted hydrocarbyl; and

X is a weakly coordinating anion;

provided that when norbornene or substituted norbornene, is present no other monomer is present.

25 128. The process as recited in claim 127 wherein said monomer is ethylene only.

129. The process as recited in claim 127 wherein said monomer is an $\alpha\text{-olefin}$ only.

130. The process as recited in claim 129 wherein said $\alpha\text{-olefin}$ is propylene.

131. The process as recited in claim 127 wherein one or more comonomer selected from the group consisting of: a compound of the formula

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 $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

- 132. The process as recited in claim 131 wherein m is 0, and R^1 is hydrocarbyl or substituted hydrocarbyl.
- 133. The process as recited in claim 127 done in the presence of a solvent.
- 134. The process as recited in claim 127 wherein R³ and R⁴ are each independently hydrogen or methyl or both R³ and R⁴ taken together are 1,8-naphthylylene, and both R² and R⁵ are 2,6-diisopropylphenyl.
 - 135. The process as recited in claim 127 used to make a block polymer.
- 15 136. The process as recited in claim 127 wherein X is BAF, SbF_6 , PF_6 , or BF_4 .
 - 137. The process as recited in claim 134 wherein X is BAF or BF4.
- 138. The process as recited in claim 137 wherein a 20 monomer is ethylene or propylene.
 - 139. The process as recited in claim 127 wherein the monomers are ethylene and propylene.
 - 140. The process as recited in claim 127 wherein said monomers are part of a crude butenes stream.
- 25 141. The process as recited in claim 127 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a carbocyclic ring.
 - 142. A polymerization process, comprising, contacting:
- a Ni[0], Pd[0] or Ni[I] compound containing a

 35 ligand which may be displaced by a ligand of the
 formula (VIII), (XXX), (XXXII) or (XXIII);
 a second compound of the formula

$$R^{28}$$
 $(CR^{30}_2)_n$ R^{29} $N=CR^{45}$ (XXX)

(XXIII)

$$\begin{array}{c|c}
R^{31} & R^{48} & R^{46} \\
\hline
R^{31} & N & N \\
R^{49} & R^{47}
\end{array}$$

or

$$\begin{array}{c|c}
R^{20} \\
O & H \\
R^{21} & N \\
R^{22} & N \\
O & H \\
R^{23}
\end{array}$$

10 (XXXII)

anion;

an oxidizing agent;
a source of a relatively weakly coordinating

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene;

5 wherein:

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 ${
m R}^2$ and ${
m R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

each R³¹ is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

 R^{44} is hydrocarbyl or substituted hydrocarbyl, and R^{28} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{44} and R^{28} taken together form a ring;

 R^{45} is hydrocarbyl or substituted hydrocarbyl, and R^{29} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{45} and R^{29} taken together form a ring;

each R^{30} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{30} taken together form a ring;

 R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

n is 2 or 3;

 ${\ensuremath{\mathbb{R}}}^{48}$ and ${\ensuremath{\mathbb{R}}}^{49}$ are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

 R^{20} and R^{23} are independently hydrocarbyl or substituted hydrocarbyl;

 R^{21} and R^{22} are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and provided that;

when norbornene or substituted norbornene is present, no other monomer is present;

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when a Pd[0] compound is used, a diene is not present; and

when said second compound is (XXX) only an Ni[0] or Ni[I] compound is used.

- 10 143. The process as recited in claim 142 wherein said monomer is ethylene only.
 - 144. The process as recited in claim 142 wherein said monomer is an $\alpha\text{-olefin}$ only.
- 145. The process as recited in claim 144 wherein said $\alpha\text{-olefin}$ is propylene.
 - 146. The process as recited in claim 142 done in the presence of a solvent.
 - 147. The process as recited in claim 142 used to make a block polymer.
- 20 148. The process as recited in claim 142 wherein the monomers are ethylene and propylene.
 - 149. The process as recited in claim 142 wherein said monomers are part of a crude butenes stream.
 - 150. The process as recited in claim 142 wherein:
- 25 R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it:

 ${\ensuremath{\mbox{R}}}^3$ and ${\ensuremath{\mbox{R}}}^4$ are each independently hydrogen,

- 30 hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring;
 - each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a
- 35 quaternary carbon atom or at least two saturated carbon atoms;

each R^{31} is independently hydrogen or hydrocarbyl;

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R⁴⁴ is hydrocarbyl, and R²⁸ is hydrogen or hydrocarbyl or R⁴⁴ and R²⁸ taken together form a ring; R⁴⁵ is hydrocarbyl, and R²⁹ is hydrogen, or hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring; each R³⁰ is independently hydrogen or hydrocarbyl, or two of R³⁰ taken together form a ring; R⁴⁶ and R⁴⁷ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^{48} and R^{49} are each independently hydrogen or hydrocarbyl;

 R^{20} and R^{23} are independently hydrocarbyl; and R^{21} and R^{22} are each in independently hydrogen or hydrocarbyl.

151. The process as recited in claim 142 wherein said olefin comprises cyclopentene.

152. A polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), oxygen, an alkyl aluminum compound, and a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

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 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

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 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

153. The process as recited in claim 152 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.

154. The process as recited in claim 152 wherein 20 said Ni[0] complex is a 1,5-cyclooctadiene complex.

155. The process as recited in claim 152 wherein said monomer is ethylene only.

156. The process as recited in claim 152 wherein said olefin comprises cyclopentene.

25 157. The process as recited in claim 152 wherein said monomer is an α -olefin only.

158. The process as recited in claim 157 wherein said $\alpha\text{-olefin}$ is propylene.

159. The process as recited in claim 152 done in 30 the presence of a solvent.

160. The process as recited in claim 156 used to make a block polymer.

161. The process as recited in claim 152 wherein the monomers are ethylene and propylene.

162. The process as recited in claim 152 wherein said monomers are part of a crude butenes stream.

163. A polymerization process, comprising, contacting oxygen and an alkyl aluminum compound, or a

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compound of the formula HX, and a compound of the formula

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

X is a weakly coordinating anion; and provided that, when norbornene or substituted norbornene is present, no other monomer is present.

164. The process as recited in claim 163 wherein \mathbb{R}^2 and \mathbb{R}^5 are each independently hydrocarbyl, provided

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that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.

- 165. The process as recited in claim 142 wherein said Ni[0] compound is bis(1,5cycloocatdiene)nickel or bis(o-tolylphosphito)nickel(ethylene) or said Pd[0] compound is tris(dibenzylideneacetone)dipalladium[0].
- 10 166. The process as recited in claim 163 wherein said monomer is ethylene only.
 - 167. The process as recited in claim 163 wherein said olefin comprises cyclopentene.
- 168. The process as recited in claim 163 wherein said monomer is an α -olefin only.
 - 169. The process as recited in claim 168 wherein said $\alpha\text{-olefin}$ is propylene.
 - 170. The process as recited in claim 163 done in the presence of a solvent.
- 20 171. The process as recited in claim 163 used to make a block polymer.
 - 172. The process as recited in claim 163 wherein the monomers are ethylene and propylene.
- 173. The process as recited in claim 163 wherein 25 said monomers are part of a crude butenes stream.
 - 174. The process as recited in claim 164 wherein said olefin comprises cyclopentene.
 - 175. The process as recited in claim 164 wherein said monomer is ethylene only.
- 30 176. A polymerization process, comprising, contacting an Ni[0] complex containing a ligand or ligands which may be displaced by (VIII), HX or a Bronsted acidic solid, and a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; and

X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

177. The process as recited in claim 176 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring.

178. The process as recited in claim 176 wherein said Ni[0] complex is bis(1,5-cycloocatidene)nickel or bis(o-tolylphosphito)nickel(ethylene)

179. The process as recited in claim 176 wherein said monomer is ethylene only.

- 180. The process as recited in claim 176 wherein said olefin comprises cyclopentene.
- 5 181. The process as recited in claim 176 wherein said monomer is an α -olefin only.
 - 182. The process as recited in claim 181 wherein said $\alpha\text{-olefin}$ is propylene.
- 183. The process as recited in claim 176 done in the presence of a solvent.
 - 184. The process as recited in claim 176 used to make a block polymer.
 - 185. The process as recited in claim 176 wherein the monomers are ethylene and propylene.
- 15 186. The process as recited in claim 176 wherein said monomers are part of a crude butenes stream.
 - 187. A process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:
- a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;
- 25 a second compound of the formula

XIX

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula

R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

M is Ni(II) or Pd(II);

5 R²⁰ and R²³ are independently hydrocarbyl or substituted hydrocarbyl;

R²¹ and R²² are each in independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R¹⁷ is independently hydrocarbyl or

10 substituted hydrocarbyl provided that any olefinic bond
in said olefin is separated from any other olefinic
bond or aromatic ring by a quaternary carbon atom or at
least two saturated carbon atoms;

Q is alkyl, hydride, chloride, iodide, or

15 bromide;

S is alkyl, hydride, chloride, iodide, or bromide;

provided that;

when norbornene or substituted norbornene is 20 present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 25 188. The process as recited in claim 187 wherein said monomer is ethylene only.
 - 189. The process as recited in claim 187 wherein said monomer is an α -olefin only.
- 190. The process as recited in claim 189 wherein 30 said α -olefin is propylene.
 - 191. The process as recited in claim 187 done in the presence of a solvent.
 - 192. The process as recited in claim 187 used to make a block polymer.
- 35 193. The process as recited in claim 191 wherein a monomer is ethylene or propylene.

194. The process as recited in claim 187 wherein the molar ratio of said first compound: said second compound (I) is about 5 to about 1000

195. The process as recited in claim 187 wherein the molar ratio of said first compound: said second compound (I) is about 10 to about 100.

196. The process as recited in claim 187 wherein the monomers are ethylene and propylene.

197. The process as recited in claim 187 wherein said monomers are part of a crude butenes stream.

198. The process as recited in claim 187 wherein R^{20} and R^{23} are independently hydrocarbyl; R^{21} and R^{22} are each in independently hydrogen or hydrocarbyl; and each R^{17} is independently hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms.

199. A process for the polymerization of olefins, comprising, contacting, at a temperature of about - 100°C to about +200°C, a compound of the formula

(XIV)

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

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 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} does not contain any olefinic bonds; and

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each R²⁷ is independently hydrocarbyl; each X is a weakly coordinating anion;

provided that, when norbornene or substituted norbornene is present, no other monomer is present.

200. The process as recited in claim 199 wherein both $\ensuremath{\text{R}^{27}}$ are methyl.

201. The process as recited in claim 199 wherein said monomer is ethylene only.

202. The process as recited in claim 199 wherein said monomer is an $\alpha\text{-olefin}$ only.

203. The process as recited in claim 202 wherein said $\alpha\text{-olefin}$ is propylene.

204. The process as recited in claim 199 wherein one or more comonomer selected from the group consisting of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1, \text{ wherein } R^1 \text{ is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.$

205. The process as recited in claim 204 wherein m is 0, and R^1 is hydrocarbyl or substituted hydrocarbyl.

206. The process as recited in claim 199 done in the presence of a solvent.

207. The process as recited in claim 199 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

208. The process as recited in claim 199 used to 35 make a block polymer.

209. The process as recited in claim 199 wherein X is BAF, SbF₆, PF₆, or BF₄.

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210. The process as recited in claim 207 wherein X is BAF or BF_4 .

- 211. The process as recited in claim 210 wherein a monomer is ethylene or propylene.
- 212. The process as recited in claim 199 wherein the monomers are ethylene and propylene.
- 213. The process as recited in claim 199 wherein said monomers are part of a crude butenes stream.
- 214. The process as recited in claim 199 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring, and each R^{17} is hydrocarbyl.
- 215. The process as recited in claim 199 wherein said olefin comprises cyclopentene.
- 216. A process for the polymerization of olefins, comprising, contacting, at a temperature of about 100°C to about +200°C:
- a first compound W, which is a neutral Lewis acid capable of abstracting either Q or S to form WQ or WS, provided that the anion formed is a weakly coordinating anion; or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion;

a second compound of the formula

(XV)

30 and one or more monomers selected from the group consisting of ethylene, an olefin of the formula

R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene; wherein:

 R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\ensuremath{R^{48}}}$ and ${\ensuremath{R^{49}}}$ are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each R31 is independently hydrocarbyl,

10 substituted hydrocarbyl, or hydrogen;

M is Ti, Zr, V, Cr, a rare earth metal, Co, Fe, Sc, Ni, or Pd of oxidation state m;

y and z are positive integers;

y+z = m;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

20 Q is alkyl, hydride, chloride, iodide, or bromide;

S is alkyl, hydride, chloride, iodide or bromide; and

provided that;

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when norbornene or substituted norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 217. The process as recited in claim 216 wherein eachR³¹ is hydrogen.
- 218. The process as recited in claim 216 wherein said monomer is ethylene only.
- 35 219. The process as recited in claim 216 wherein said monomer is an α -olefin only.
 - 220. The process as recited in claim 219 wherein said α -olefin is propylene.

221. The process as recited in claim 216 done in the presence of a solvent.

- 222. The process as recited in claim 216 wherein R^{48} and R^{49} are each independently hydrogen or methyl,
- 5 both R^{46} and R^{47} are 2,6-diisopropylphenyl, and T^1 is methyl.
 - 223. The process as recited in claim 216 used to make a block polymer.
- 224. The process as recited in claim 216 wherein M 10 is Ni(II).
 - 225. The process as recited in claim 216 wherein M is Pd(II).
 - 226. The process as recited in claim 225 wherein a monomer is ethylene or propylene.
- 15 227. The process as recited in claim 216 wherein: M is Ti(IV), Q and S are chloride, and y and z are 2;
 - M is Zr(IV), Q and S are chloride, and y and z are 2;
- 20 M is Co(II), Q and S are bromide, and y and z are 1;
 - M is Fe(II), Q and S are chloride, and y and z are 1;
- M is Sc(III), Q and S are chloride, y is 1 and z 25 is 2;
 - M is Ni(II), Q and S are bromide or chloride, and y and z are 1; M is Pd(II), Q and S are methyl, and y and z are 1;
- M is Ni(I), Q is methyl, chloride, bromide, iodide or acetylacetonate, y is 1, and z is 0;

or

- M is Ni(II), Q and S are methyl, and y and z are 1.
- 228. The process as recited in claim 216 wherein the monomers are ethylene and propylene.
 - 229. The process as recited in claim 216 wherein said monomers are part of a crude butenes stream.

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230. The process as recited in claim 216 wherein: R^{46} and R^{47} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\mbox{R}}^{48}$ and ${\mbox{R}}^{49}$ are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

each R³¹ is independently hydrocarbyl, substituted hydrocarbyl, or hydrogen; and each R¹⁷ is hydrocarbyl.

231. The process as recited in claim 216 wherein said olefin comprises cyclopentene.

232. A compound of the formula

wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

X is a weakly coordinating anion; and

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

provided that when R^3 and R^4 taken together are hydrocarbylene to form a carbocyclic ring Z is not an organic nitrile.

233. The compound as recited in claim 232 wherein T^1 is methyl, and Z is $R^6{}_2O$ or R^7CN wherein each R^6 independently hydrogen or hydrocarbyl and R^7 is hydrocarbyl.

10 234. The compound as recited in claim 232 wherein \mathbb{R}^3 and \mathbb{R}^4 are each independently hydrogen or methyl or \mathbb{R}^3 and \mathbb{R}^4 taken together are 1,8-naphthylylene, and both \mathbb{R}^2 and \mathbb{R}^5 are 2,6-diisopropylphenyl.

235. The compound as recited in claim 233 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl, and wherein X is BAF, SbF₆, PF₆, or BF₄.

236. The compound as recited in claim 232 wherein X is BAF , SbF $_{\!6}$, PF $_{\!6}$, or BF $_{\!4}$.

237. The compound as recited in claim 232 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a carbocyclic ring.

238. The compound as recited in claim 232 wherein each of R^2 , R^3 , R^4 , R^5 , T^1 , Z, and X are as follows:

R ²	R ³	R4.	R ⁵	T	z	х
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Ме	OEt ₂	BAF
2,6-i-PrPh	н	H	2,6-i-PrPh	Me	OEt ₂	BAF
2,6-MePh	н	н	2,6-MePh	Me	OEt ₂	BAF
2,6-MePh	Me ·	Me	2,6-MePh	Me	OEt ₂	BAF
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt ₂	SbF ₆
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt ₂	BF4
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	OEt ₂	PF ₆
2,6-i-PrPh	H	н	2,6-i-PrPh	Me	OEt ₂	SbF ₆
2,4,6-MePh	Me	Me	2,4,6-MePh	Me	OEt ₂	SbF ₆
2,6-i-PrPh	An	An	2,6-i-PrPh	Me	OEt ₂	SbF6
2,6-i-PrPh	Me	Me	2,6-i-PrPh	Me	NCMe	SbF ₆
Ph	Me	Me	Ph	Me	NCMe	SbF ₆
2,6-EtPh	Me	Me	2,6-EtPh	Me	NCMe	BAF
2,6-EtPh	Me	Me	2,6-EtPh	Me	NCMe	SbF ₆
2-t-BuPh	Me	Me	2-t-BuPh	Me	NCMe	SbF ₆
1-Np	Me	Me	1-Np	Me	NCMe	SbF ₆
Ph ₂ CH	н	н	Ph ₂ CH	Me	NCMe	SbF ₆
2-PhPh	Me	Me	2-PhPh	Me	NCMe	SbF ₆
Ph	a	а	Ph	Me	NCMe	BAF
Ph	Me	Me	Ph	Me	NCMe	SbF ₆
Ph	Ph	Ph	Ph	Me	NCMe	BAF
Ph ₂ CH	н	н	Ph ₂ CH	Me .	NCMe .	SbF ₆
Ph ₂ CH	н	н	Ph ₂ CH	Me	SMe ₂	SbF ₆
a - CMe ₂ CH ₂ CMe ₂						

239. A compound of the formula

wherein:

 R^{50} is substituted phenyl; R^{51} is phenyl or substituted phenyl;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

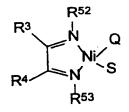
and provided that groups in the 2 and 6 positions of R^{50} have a difference in $E_{\rm s}$ of about 0.15 or more.

240. The compound as recited in claim 239 wherein groups in the 2 and 6 of R^{51} have a difference in $E_{\rm s}$ of about 0.60 or more.

241. The compound as recited in claim 239 wherein the group in the 2 position of R^{50} is t-butyl and the group in 6 position of R^{50} is methyl or hydrogen.

242. The compound as recited in claim 241 wherein the group in the 2 position of R^{51} is t-butyl and the group in 6 position of R^{51} is methyl or hydrogen.

243. A compound of the formula



(XXXVI)

20 wherein:

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R⁵² is substituted phenyl;

R⁵³ is phenyl or substituted phenyl;

 ${
m R}^3$ and ${
m R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${
m R}^3$ and ${
m R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

Q is alkyl, hydride, chloride, bromide or iodide;

S is alkyl, hydride, chloride, bromide or

30 iodide;

and provided that;

groups in the 2 and 6 positions of R^{52} have a difference in $E_{\rm s}$ of 0.15 or more; and

except when M is Pd, when both Q and S are each independently chloride, bromide or iodide W is capable of transferring a hydride or alkyl group to M.

- 244. The compound as recited in claim 243 wherein 5 said difference is about 0.20 more.
 - 245. The compound as recited in claim 243 wherein groups in the 2 and 6 of R^{51} have a difference in $E_{\rm s}$ of 0.15 or more.
- 246. The compound as recited in claim 243 wherein 10 the group in the 2 position of R⁵² is i-propyl or t-butyl and the group in the 6 position of R⁵² is methyl or hydrogen.

247. The compound as recited in claim 246 wherein the group in the 2 position of R^{53} is i-propyl or t-butyl and the group in 6 position of R^{52} is methyl or hydrogen.

248. A compound of the formula

wherein:

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R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

T¹ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -;

R¹⁵ is hydrocarbyl not containing an olefinic or acetylenic bond;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound is less than about 6;

 \mathbf{X}^{T} is a weakly coordinating anion.

249. The compound as recited in claim 248 wherein T^1 is methyl, Z is $R^6{}_2\text{O}$ wherein each R^6 is independently alkyl, and X is BAF, SbF₆, PF₆, or BF₄.

250. The compound as recited in claim 248 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

251. The compound as recited in claim 249 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

252. The compound as recited in claim 248 wherein R^2 and R^5 are each independently hydrocarbyl provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

253. A compound of the formula

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(IV)

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wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

M is Ni(II) or Pd(II);

each R^{16} is independently hydrogen or alkyl containing 1 to 10 carbon atoms;

n is 1, 2, or 3;

 X^{-} is a weakly coordinating anion; and

R⁸ is hydrocarbyl.

254. The compound as recited in claim 253 wherein R^3 and R^4 are each independently hydrogen or methyl, both R^2 and R^5 are 2,6-diisopropylphenyl, M is Pd(II), and X is BAF, SbF₆, PF₆, or BF₄.

20 255. The compound as recited in claim 254 wherein each R¹⁶ is hydrogen and n is 3.

256. The compound as recited in claim 253 wherein M is Pd(II).

257. The compound as recited in claim 253 wherein each R^{16} is hydrogen and n is 3.

258. The compound as recited in claim 253 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

259. A compound of the formula

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$$\begin{array}{c|cccc}
R^3 & R^2 & R^2 & R^3 \\
\hline
 & N & T^1 & R^2 & R^3 \\
\hline
 & N & R^4 & R^5 & R^4 & X^5
\end{array}$$

$$\begin{array}{c|ccccc}
 & R^2 & R^3 & R^3 & R^3 & R^4 & R^5 & R^4 & R^5 & X^5 & R^4 & X^5 & R^5 & X^5 & R^4 & X^5 & R^5 & X^5 & R^4 & X^5 & R^5 & X^5 & R^6 & X^5 &$$

wherein:

 ${\ R}^2$ and ${\ R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

E is halogen or -OR18;

R¹⁸ is hydrocarbyl not containing olefinic or acetylenic bonds;

T¹ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, R¹⁵C(=0) - or R¹⁵OC(=0) -;

 $\ensuremath{\text{R}^{\text{15}}}$ is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion.

260. The compound as recited in claim 259 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

261. The compound as recited in claim 259 wherein T^1 is methyl, and E is chlorine:

30 262. The compound as recited in claim 261 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

263. The compound as recited in claim 262 Wherein X is BAF, SbF₆, PF₆, or BF₄.

264. A compound of the formula $[(\eta^4-1,5-COD)PdT^1Z]^+X^-$, wherein:

T¹ is hydrocarbyl not containing olefinic or acetylenic bonds;

X is a weakly coordinating anion;

COD is 1,5-cyclooctadiene;

Z is R¹⁰CN; and

10 R¹⁰ is hydrocarbyl not containing olefinic or acetylenic bonds.

265. The compound as recited in claim 264 wherein T^1 is methyl.

266. The compound as recited in claim 265 wherein Z is methyl and X is BAF, SbF₆, PF₆, or BF₄.

267. A compound of the formula

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wherein:

M is Ni(II) or Pd(II);

 ${\rm R}^2$ and ${\rm R}^5$ are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

 T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH2CH2CH2CO2R8;

P is a divalent group containing one or more repeat units derived from the polymerization of one or more of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene and, when M is Pd(II), optionally one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, CO, or a vinyl ketone;

10 R⁸ is hydrocarbyl;

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m is 0 or an integer from 1 to 16;

 ${\ensuremath{\mathbb{R}}}^1$ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion.

15 268. The compound as recited in claim 267 wherein \mathbb{R}^1 is hydrocarbyl or substituted hydrocarbyl.

269. The compound as recited in claim 267 wherein T^3 is hydrogen or alkyl.

270. The compound as recited in claim 267 wherein M is Pd(II).

271. The compound as recited in claim 269 wherein M is Pd(II).

272. The compound as recited in claim 267 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

273. The compound as recited in claim 271 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

274. The compound as recited in claim 267 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring.

275. A compound of the formula

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wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^2 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, hydrocarbyl substituted with keto or ester groups but not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

 ${\rm R}^{15}$ is hydrocarbyl not containing olefinic or acetylenic bonds; and

X is a weakly coordinating anion.

276. The compound as recited in claim 275 wherein \mathbf{T}^2 is methyl.

277. The compound as recited in claim 276 wherein R^3 and R^4 are each independently hydrogen or methyl or R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.

278. The compound as recited in claim 276 wherein X is BAF, SbF_6 , PF_6 , or BF_4 .

279. The compound as recited in claim 275 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3

and R^4 taken together are hydrocarbylene to form a ring.

280. A process for the production of polyolefins, comprising, contacting, at a temperature of about - 100°C to about +200°C, a compound of the formula

with one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

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M is Ni(II) or Pd(II);

 R^2 and R^5 are hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1;$

T³ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH₂CH₂CH₂CO₂R⁸;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and, when M is Pd(II),

optionally one or more of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, CO, or a vinyl ketone;

R⁸ is hydrocarbyl;

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each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion; provided that when norbornene or substituted

norbornene is present no other monomer is present;

when M is Pd a diene is not present; and further provided that when M is Ni(II) R^{11} is not $-CO_2R^8$.

281. The compound as recited in claim 280 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and each R^{17} is hydrocarbyl.

282. The process as recited in claim 280 wherein T^3 is methyl.

283. The process as recited in claim 282 wherein said monomer is ethylene only, and R¹¹ is hydrogen.

284. The process as recited in claim 282 wherein said monomer is an α -olefin only, and R¹¹ is alkyl.

285. The process as recited in claim 284 wherein said $\alpha\text{-olefin}$ is propylene, and R^{11} is methyl.

286. The process as recited in claim 280 wherein M is Pd(II), and one or more comonomers selected from the group consisting of: a compound of the formula $CH_2=CH\left(CH_2\right)_mCO_2R^1, \text{ wherein } R^1 \text{ is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon}$

atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

- 287. The process as recited in claim 286 wherein m is 0, and R^1 is hydrocarbyl or substituted hydrocarbyl.
- 288. The process as recited in claim 287 wherein m is 0, and \mathbb{R}^1 is hydrocarbyl or substituted hydrocarbyl.
- 289. The process as recited in claim 280 done in the presence of a solvent.
- 290. The process as recited in claim 280 done in 10 the absence of a solvent.
 - 291. The process as recited in claim 282 wherein R^3 and R^4 are each independently hydrogen or methyl or R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.
- 15 292. The process as recited in claim 280 used to make a block polymer.
 - 293. The process as recited in claim 280 wherein X is BAF, SbF₆, PF₆, or BF₄.
- 294. The process as recited in claim 291 wherein 20 \times is BAF, SbF₆, PF₆, or BF₄.
 - 295. The process as recited in claim 294 wherein a monomer is ethylene or propylene.
 - 296. The process as recited in claim 280 wherein the monomers are ethylene and propylene.
- 25 297. The process as recited in claim 280 wherein said monomers are part of a crude butenes stream.
 - 298. The process as recited in claim 280 wherein said monomers comprise cyclopentene.
- 299. A process for the production of polyolefins, 30 comprising, contacting, at a temperature of about 100°C to about +200°C, a compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${
m R}^3$ and ${
m R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or ${
m R}^3$ and ${
m R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{11} is independently hydrogen or alkyl, or both of R^{11} taken together are hydrocarbylene to form a carbocyclic ring;

 T^3 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or $-CH_2CH_2CH_2CO_2R^8\,;$ Q is a monoanion;

P is a divalent group containing one or more

repeat units derived from the polymerization of one or
monomers selected from the group consisting of
ethylene, an olefin of the formula R¹⁷CH=CH₂ or
R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted
norbornene, and norbornene, and, when M is Pd(II),
optionally one or more of: a compound of the formula
CH₂=CH(CH₂)_mCO₂R¹, CO, or a vinyl ketone;

R⁸ is hydrocarbyl;

a is 1 or 2; y + a + 1 = m;

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each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R¹ is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16;

and X is a weakly coordinating anion;
provided that, when norbornene or substituted
norbornene is present, no other monomer is present;

when M is Pd a diene is not present; and further provided that, when M is Ni(II), T³ is not - CH₂CH₂CO₂R⁸.

300. The process as recited in claim 299 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and each R^{17} is hydrocarbyl.

301. The process as recited in claim 299 wherein T^3 is methyl.

302. The process as recited in claim 301 wherein said monomer is ethylene only, and R^{11} is hydrogen.

303. The process as recited in claim 301 wherein said monomer is an α -olefin only, and R^{11} is alkyl.

304. The process as recited in claim 303 wherein said α -olefin is propylene, and each R^{11} is methyl or hydrogen.

305. The process as recited in claim 299 wherein M is Pd(II), and one or more comonomer selected from the group consisting of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon

atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

306. The process as recited in claim 305 wherein m is 0, and R^1 is hydrocarbyl or substituted hydrocarbyl.

- 307. The process as recited in claim 299 done in the presence of a solvent.
- 308. The process as recited in claim 299 done in the absence of a solvent.
- 309. The process as recited in claim 301 wherein $10 ext{ R}^3$ and $ext{R}^4$ are each independently hydrogen or methyl, and both $ext{R}^2$ and $ext{R}^5$ are 2,6-disopropylphenyl.
 - 310. The process as recited in claim 299 used to make a block polymer.
- 311. The process as recited in claim 299 wherein X is BAF, SbF_6 , PF_6 , or BF_4 .
 - 312. The process as recited in claim 309 wherein X is BAF, SbF_6 , PF_6 , or BF_4 .
 - 313. The process as recited in claim 312 wherein a monomer is ethylene or propylene.
- 20 314. The process as recited in claim 299 wherein the monomers are ethylene and propylene.
 - 315. The process as recited in claim 299 wherein said monomers are part of a crude butenes stream.
- 316. The process as recited in claim 299 wherein 25 said monomer comprises cyclopentene.
 - 317. A compound of the formula

$$R^{3}$$
 N
 $(Q)_{y}$
 H
 $C-R^{1}$
 N
 $H-C-R^{1}$
 R^{5}
 PT^{3}
 (XVI)
 $(X^{3})_{a}$

30 wherein:

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M is Zr, Ti, Sc, V, Cr, a rare earth metal, Fe, Co, Ni or Pd of oxidation state m;

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R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it:

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R11 is independently hydrogen, or alkyl, or both of R11 taken together are hydrocarbylene to form a carbocyclic ring;

T³ is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, or -CH2CH2CH2CO2R8;

P is a divalent group containing one or more repeat units derived from the polymerization of one or monomers selected from the group consisting of ethylene, an olefin of the formula R17CH=CH2 or R¹⁷CH=CHR¹⁷, cyclopentene, cyclobutene, substituted norbornene, and norbornene, and optionally, when M is Pd(II), one or more of: a compound of the formula CH₂=CH(CH₂)_mCO₂R¹, CO, or a vinyl ketone;

Q is a monovalent anion; R⁸ is hydrocarbyl; a is 1 or 2;

v + a + 1 = m;

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each R17 is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms;

R1 is hydrogen, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

m is 0 or an integer of 1 to 16; and and X is a weakly coordinating anion;

and provided that when M is Pd a diene is not 35 present;.

318. The compound as recited in claim 317 wherein R1 is hydrocarbyl or substituted hydrocarbyl.

319. The compound as recited in claim 317 wherein T^3 is hydrogen or alkyl.

320. The compound as recited in claim 317 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and each R^{17} is hydrocarbyl.

321. The compound as recited in claim 317 wherein M is Pd(II).

322. The compound as recited in claim 319 wherein M is Pd(II).

323. The compound as recited in claim 317 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

324. The compound as recited in claim 317 wherein both of R^{11} taken together form a five-membered carbocyclic ring.

325. The compound as recited in claim 317 wherein both of R^{11} taken together are hydrocarbylene to form a carbocyclic ring.

326. A process, comprising, contacting, at a temperature of about -40°C to about $+60^{\circ}\text{C}$, a compound of the formula $[(\eta^4-1,5-\text{COD})\,\text{PdT}^1\text{Z}]^+\text{X}^-$ and a diimine of the formula

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to produce a compound of the formula

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wherein:

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

X is a weakly coordinating anion;

COD is 1,5-cyclooctadiene;

Z is R¹⁰CN;

10 R¹⁰ is hydrocarbyl not containing olefinic or acetylenic bonds;

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

327. The process as recited in claim 326 wherein R^{10} is alkyl, and T^{1} is methyl.

328. The process as recited in claim 326 carried out in a solvent of the formula R¹⁰CN, wherein R¹⁰ is hydrocarbyl not containing olefinic or acetylenic bonds.

329. The process as recited in claim 327 wherein R^3 and R^4 are each independently hydrogen or methyl, and both R^2 and R^5 are 2,6-diisopropylphenyl.

330. The process as recited in claim 326 wherein X is BAF, SbF $_6$, PF $_6$, or BF $_4$.

331. The process as recited in claim 326 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

332. An ethylene homopolymer with a density of 0.86 g/ml or less.

333. The ethylene homopolymer as recited in claim 332 wherein said density is about 0.85 or less.

334. A compound of the formula

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(XIV)

wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R²⁷ is hydrocarbyl; and each X is a weakly coordinating anion.

335. The compound as recited in claim 334 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3

and R^4 taken together are hydrocarbylene to form a ring.

336. The compound as recited in claim 334 wherein both of R^{27} are methyl.

337. The compound as recited in claim 334 wherein R^3 and R^4 are each independently hydrogen or methyl or R^3 and R^4 taken together are 1,8-naphthylylene, and both R^2 and R^5 are 2,6-diisopropylphenyl.

338. The compound as recited in claim 334 wherein 10 $\,$ X is BAF, SbF₆, PF₆, or BF₄.

339. A compound of the formula

wherein:

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M is Ni(II) or Pd(II);

 $\rm R^2$ and $\rm R^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{14} is independently hydrogen, alkyl or $-(CH_2)_mCO_2R^1$;

 R^1 is hydrogen, or hydrocarbyl or substituted 30 hydrocarbyl containing 1 to 10 carbon atoms; $T^4 \text{ is alkyl, } -R^{60}C(0)OR^8, \ R^{15}(C=0) - \text{ or } R^{15}OC(=0) - C$

R¹⁵ is hydrocarbyl not containing olefinic or acetylenic bonds;

 ${\ensuremath{\mathsf{R}}}^{60}$ is alkylene not containing olefinic or acetylenic bonds;

R⁸ is hydrocarbyl;;

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and X is a weakly coordinating anion; and provided that when R^{14} is $-(CH_2)_mCO_2R^1$, or T^4 is not alkyl, M is Pd(II).

340. The compound as recited in claim 339 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring.

- 341. The compound as recited in claim 339 wherein T^4 is methyl and M is Pd(II).
- 342. The compound as recited in claim 339 wherein each R^{14} is independently hydrogen or $-(CH_2)_mCO_2R^1$ and M is Pd(II).
- 343. A homopolypropylene with a glass transition temperature of -30°C or less, provided that said homopolypropylene has at least 50 branches per 1000 methylene groups.
- 344. The homopolypropylene as recited in claim 343 wherein said glass transition temperature is about 35°C or less.
- 345. A homopolymer of cyclopentene having a degree of polymerization of about 30 or more and an end of melting point of about 100°C to about 320°C, provided that said homopolymer has less than 5 mole percent of enchained linear olefin containing pentylene units.
- 346. The homopolymer as recited in claim 345 wherein at least 90 percent of repeat units are 1,3-cyclopentylene repeat units.
- 347. The homopolymer as recited in claim 345 wherein at least 90 percent of repeat units are cis-1,3-cyclopentylene repeat units.

348. The homopolymer as recited $\tilde{\text{in}}$ $\tilde{\text{claim}}$ 345 wherein an X-ray powder diffraction pattern thereof has reflections at approximately 17.3°, 19.3°, 24.2°, and 40.7° 20.

- 349. A homopolymer of cyclopentene that has an X-ray diffraction pattern with reflections at approximately 17.3°, 19.3°, 24.2°, and 40.7° 2θ.
 - 350. The homopolymer as recited in claim 349 which has a monoclinic unit cell of the approximate dimensions: a=0.561 nm; b=0.607 nm; c=7.37 nm; and $q=123.2^{\circ}$.
 - 351. The homopolymer as recited in claim 349 wherein at least 90 percent of repeat units are 1,3-cyclopentylene repeat units.

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- 15 352. The homopolymer as recited in claim 351 wherein at least 90 percent of repeat units are cis-1,3-cyclopentylene repeat units.
 - 353. A homopolymer of cyclopentene wherein at least 90 mole percent of enchained cyclopentylene units are 1,3-cyclopentylene units, and said homopolymer has an average degree of polymerization of 30 more.
 - 354. A homopolymer of cyclopentene wherein at least 90 mole percent of enchained cyclopentylene units are cis-1,3-cyclopentylene, and said homopolymer has an average degree of polymerization of about 10 or more.
 - 355. A copolymer of cyclopentene and ethylene wherein at least 75 mole percent of enchained cyclopentylene units are 1,3-cyclopentylene units.
- 356. The copolymer as recited in claim 355 wherein 30 at least 50 mole percent of the repeat units are derived from cyclopentene.
 - 357. The copolymer as recited in claim 355 wherein there are at least 20 branches per 1000 methylene carbon atoms.
- 35 358. A copolymer of cyclopentene and ethylene wherein there are at least 20 branches per 1000 methylene carbon atoms.

359. The copolymer as recited in claim 358 wherein at least 50 mole percent of the repeat units are derived from ethylene.

- 360. A copolymer of cyclopentene and ethylene wherein at least 50 mole percent of the repeat units are derived from cyclopentene.
 - 361. A copolymer comprising repeat units of cyclopentene and an $\alpha\text{-olefin}$.

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- 362. The copolymer as recited in claim 361 wherein repeat units derived from ethylene are also present.
 - 363. The copolymer as recited in claim 361 wherein said $\alpha\text{-olefin}$ is a linear $\alpha\text{-olefin}$.
 - 364. The copolymer as recited in claim 361 wherein at least 90 mole percent of repeat units derived from cyclopentene are 1,3-cyclopentylene units.
 - 365. The copolymer as recited in claim 364 wherein at least 90 mole percent of repeat units derived from cyclopentene are cis-1,3-cyclopentylene units.
 - 366. A fiber made from the polymer of claim 345, 349, 353, 354, 355, 356, 357, 358, 360 or 361.
 - 367. A polymerization process, comprising, contacting an olefin of the formula R¹⁷CH=CH₂ or R¹⁷CH=CHR¹⁷, each R¹⁷ is independently hydrogen, hydrocarbyl, or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms with a catalyst, wherein said catalyst:

contains a nickel or palladium atom in a 30 positive oxidation state;

contains a neutral bidentate ligand coordinated to said nickel or palladium atom, and wherein coordination to said nickel or palladium atom is through two nitrogen atoms or a nitrogen atom and a phosphorous atom; and

said neutral bidentate ligand, has an Ethylene Exchange Rate of less than 20,000 L-mol⁻¹s⁻¹ when said catalyst contains a palladium atom, and less than

50,000 L-mol⁻¹s⁻¹ when said catalyst contains a nickel atom:

and provided that when M is Pd a diene is not present.

368. The polymerization process as recited in claim 367 wherein said Ethylene Exchange Rate is less than 10,000 L-mol⁻¹s⁻¹ when said catalyst contains a palladium atom, and less than 25,000 L-mol⁻¹s⁻¹ when said catalyst contains a nickel atom.

369. The process as recited in claim 367 wherein said bidentate ligand is coordinated to said nickel or palladium atom through two nitrogen atoms.

370. The process as recited in claim 369 wherein said ligand is an α -diimine.

371. The process as recited in claim 367 wherein said olefin has the formula $R^{17}CH=CH_2$, wherein R^{17} is hydrogen or n-alkyl.

372. A process for the polymerization of olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

a first compound which is a source of a relatively noncoordinating monoanion;

a second compound of the formula

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, or norbornene;

wherein:

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

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each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that R^{17} does not contain any olefinic bonds;

 T^1 is hydrogen, hydrocarbyl not containing olefinic or acetylenic bonds, $R^{15}C(=0)$ - or $R^{15}OC(=0)$ -;

S is chloride, iodide, or bromide; and provided that, when norbornene or substituted norbornene is present, no_other monomer is present.

373. The process as recited in claim 372 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and each R^{17} is saturated hydrocarbyl.

374. The process as recited in claim 372 wherein said source is an alkali metal salt of said anion.

375. The process as recited in claim 372 wherein \mathbf{T}^{1} is methyl.

376. The process as recited in claim 372 wherein said monomer is ethylene only, and R^{11} is hydrogen.

377. The process as recited in claim 372 wherein one or more comonomer selected from the group consisting of: a compound of the formula $CH_2=CH(CH_2)_mCO_2R^1$, wherein R^1 is hydrogen or, hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms, and m is 0 or an integer of 1 to 16; CO; and a vinyl ketone is also present.

378. The process as recited in claim 372 done in the presence of a solvent.

379. The process as recited in claim 368 used to make a block polymer.

- 380. The process as recited in claim 368 wherein said monoanion is BAF, SbF₆, PF₆, or BF₄.
- 381. The process as recited in claim 374 wherein said monoanion is BAF, SbF₆, PF₆, or BF₄.
 - 382. The process as recited in claim 377 wherein a monomer is ethylene or propylene.
- 383. The process as recited in claim 372 wherein the monomers are ethylene and propylene.
 - 384. A polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH\left(CH_2\right)_eG$ by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or -CO₂R¹; each e is independently 0 or an integer of 1 to 20;

each R¹ is independently hydrogen, hydrocarbyl 20 or substituted hydrocarbyl;

and provided that:

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said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G
25 is hydrogen;

except when no branches should be theoretically present, the number of branches per 1000 methylene groups is 90% or less than the number of theoretical branches per 1000 methylene groups, or the number of branches per 1000 methylene groups is 110% or more of theoretical branches per 1000 methylene groups; and

when there should be no branches theoretically present, said polyolefin has 50 or more branches per 1000 methylene groups;

and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

wherein except when no branches should be theoretically present the number of branches per 1000 methylene groups is 80% or less than the number of theoretical branches per 1000 methylene groups, or the number of branches per 1000 methylene groups is 120% or more of theoretical branches per 1000 methylene groups is 120% or more of theoretical branches per 1000 methylene groups; and

when there should be no branches theoretically present, said polyolefin has 75 or more branches per 1000 methylene groups.

386. A polyolefin, comprising, a polymer made by polymerizing one or more monomers of the formula $H_2C=CH(CH_2)_eG$ by contacting said monomers with a transition metal containing coordination polymerization catalyst, wherein:

each G is independently hydrogen or -CO₂R¹; each e is independently 0 or an integer of 1 to 20;

R¹ is independently hydrogen, hydrocarbyl or 20 substituted hydrocarbyl;

and provided that:

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said polymer has at least 50 branches per 1000 methylene groups;

in at least 50 mole percent of said monomers G is hydrogen;

said polymer has at least 50 branches of the formula $-(CH_2)_f G$ per 1000 methylene groups, wherein when G is the same as in a monomer and e $\neq f$, and/or for any single monomer of the formula $H_2C=CH(CH_2)_e G$ there are less than 90% of the number of theoretical branches per 1000 methylene groups, or more than 110% of the theoretical branches per 1000 methylene groups of the formula $-(CH_2)_f G$ and f=e, and wherein f is 0 or an integer of 1 or more;

and provided that said polyolefin has at least two branches of different lengths containing less than 6 carbon atoms each.

387. The polyolefin as recited in claim 386 wherein when G is the same as in a monomer and e \neq f, and/or for any single monomer of the formula $H_2C=CH(CH_2)_eG$ there are less than 80% of the number of theoretical branches per 1000 methylene groups, or more than 120% of the theoretical branches per 1000 methylene groups of the formula -(CH₂)_fG and f=e.

388. A tackifier for an adhesive comprising the polymer of claim 1, 2, 3, 5, 6 or 7.

389. An oil additive for smoke suppression in twostroke gasoline engines comprising the polymer of claim 1, 2, 3, 4, 5, 6, or 7.

390. A base resin for a hot melt adhesive, a pressure sensitive adhesive or a solvent applied adhesive comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

391. A viscosity modifier for lubricating oils comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

392. A coating or penetrant comprising the polymer of claim 1, 2, 4, 5, 6 or 7.

393. A base polymer for caulking comprising the polymer of claim 1, 2, 3, 4, 5, 6 or 7.

394. The polymer of claim 1, 2, 4, 5, 6 or 7 which is grafted so it contains functional groups.

25 395. A toughener for a thermoplastic or a thermoset comprising the polymer of claim 14.

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396. A modifier for asphalt comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

397. The polymer of claim 1, 3, 4, 6, 7, 332 or 30 343 which is chlorinated or chlorosulfonated.

398. The polymer of claim 17 which is elastomeric.

399. A wire insulation or jacketing comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

400. A toughener for polyolefins comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

401. A base for a synthetic lubricant comprising the polymer of claim 1, 4, 6, 7, 332 or 343.

402. A drip suppressant for synthetic polymers comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

- 403. A blown or cast film, or a sheet comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 404. An additive for wax candles for smoke suppression or drip control comprising the polymer of claim 1, 4, 6, 7, 332 or 343.
- 405. A base resin for carpet backing comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 406. A capliner resin comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 407. A thermal transfer imaging resin comprising the polymer of claim 1, 4, 6, 7, 332 or 343.
- 15 408. An extrusion or coextrusion onto a plastic, metal, textile or paper web comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 409. A laminating adhesive for glass comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
- 20 410. A foamed object comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 411. A powder used to coat an object comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 412. A hose comprising the polymer of claim 1, 3,
- 25 4, 6, 7, 332 or 343.
 - 413. A pour point depressant for a fuel or oil comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
- 414. A nonwoven fabric comprising the polymer of 30 claim 1, 3, 4, 6, 7, 332 or 343.
 - 415. A roofing membrane comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 416. A reactive diluent for an automotive finish comprising the polymer of claim 7, 8, 9, 10, 11 or 12.
- 35 417. An ionomer comprising the polymer of claim 7, 8, 9, 10, 11 or 12.
 - 418. A molding resin comprising the ionomer of claim 417.

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419. A core for the initiation of condensation polymerizations yielding a grafted branched polymer, comprising the polymer of claim 7, 8, 9, 10, 11, or 12.

- 420. A compatiblizing agent comprising the polymer of claim 3, 6 or 7.
 - 421. A toughener for a thermoplastic or thermoset comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
- 422. An internal plasticizer for polymers
 10 comprising the polymer of claim 1, 3, 4, 6, 7, 332 or
 343.
 - 423. An adhesive for adhering a polymer comprising the polymer of claim 3, 6, 7, 332 or 343.
- 424. A curing agent for a polymer containing
 15 complimentary functional groups comprising the polymer of claim 3, 6 or 7.
 - 425. An additive to thermoplastic polymers to improve the adhesion of paint thereto comprising the polymer of claim 3, 6 or 7.
- 20 426. A polymer blend comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343 and at least one other polymer.
- 427. A polymer of one or more alpha-olefins of the formula $CH_2=CH(CH_2)$ aH wherein a is an integer of 2 or more, which contains the structure

$$R^{35}$$
 R^{36} (XXV)

- wherein R^{35} is an alkyl group and R^{36} is an alkyl group containing two or more carbon atoms, and provided that R^{35} is methyl in at least about 2 mole percent of the total amount of (XXV) in said polymer.
 - 428. The polymer as recited in claim 427 wherein a structure in which \mathbb{R}^{35} is methyl is about 5 mole percent or more of the total amount of (XXV) in said polymer.

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- 429. The polymer as recited in claim 427 wherein a structure in which \mathbb{R}^{35} is methyl is about 50 mole percent or more of the total amount of (XXV) in said polymer.
- 430. A polymer of one or more alpha-olefins of the formula $CH_2=CH(CH_2)_aH$ wherein a is an integer of 2 or more, wherein said polymer contains methyl branches and said methyl branches are about 25 to about 75 mole percent of the total branches in said polymer.
- 10 431. The polymer as recited in claim 430 which contains branches of the formula -(CH₂)_aH.
 - 432. The polymer as recited in claim 430 which contains branches of the formula $-(CH_2)_nH$ wherein n is an integer of 6 or greater.
 - 433. The polymer as recited in claim 431 which contains the structure

$$CH_3$$

 $-CH_2-CH-(CH_2)_aH$ (XXVI)

and wherein (XXVI) is present in an amount of 0.5 branches of (XXVI) or more per 1000 methylene atoms greater than can be accounted for by end groups.

434. A polyethylene containing the structure (XXVII) in an amount greater than can be accounted for by end groups.

- 435. The polyethylene as recited in claim 434 which contains about 2 or more of (XXVII) per 1000 methylene groups in said polymer.
- 436. A polypropylene containing one or both of the structures (XXVIII) and (XXIX), provided that:
- (XXIX), if present is present in an amount greater than or equal to 0.5 of (XXIX) per 1000

methylene groups greater than can be accounted for by end groups;

or the polymer contains at least 0.5 or more of (XXVIII) per 1000 methylene groups, if (XXVIII) is present.

$$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 \\ \mid \\ \text{CH}_{-} \\ \text{CH}_3 \\ \mid \\ \text{CH}_2\text{CH}_2\text{-CH-CH}_3 \end{array} (XXIX)$$

10 437. The polypropylene as recited in claim 436 which contains about 15 or more groups of structure (XXVIII) per 1000 methylene groups in said polypropylene.

438. The polypropylene as recited in claim 436 which contains about 15 or more groups of structure (XXIX) per 1000 methylene groups in said polypropylene.

439. A process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

20 ethylene;

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a first compound W, which is a neutral Lewis acid capable of abstracting X to form WX, provided that the anion formed is a weakly coordinating anion, or a cationic Lewis or Bronsted acid whose counterion is a weakly coordinating anion; and

a second compound of the formula

(XXXI)

wherein:

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl;

 R^3 and R^4 are each independently hydrogen, substituted hydrocarbyl, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring; and

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Q and S are each independently chlorine, bromine, iodine or alkyl; and

wherein an α -olefin containing 4 to 40 carbon 10 atoms is produced.

- 440. The process as recited in claim 439 wherein said linear α -olefin has the formula $H_2C=CHR^1$, wherein R^1 is n-alkyl containing 2 to 30 carbon atoms.
- 441. The process as recited in claim 439 wherein $5 \quad R^2$ and R^5 are phenyl.
 - 442. The process as recited in claim 439 wherein ${\bf R}^3$ and ${\bf R}^4$ are hydrogen, methyl or 1,8-naphthylylene.
 - 443. The process as recited in claim 440 wherein \mathbb{R}^3 and \mathbb{R}^4 are hydrogen, methyl or 1,8-naphthylylene.
- 20 444. The process as recited in claim 439 wherein said second compound is an alkyl aluminum compound.
 - 445. The process as recited in claim 444 wherein said alkyl aluminum compound is R⁹₃Al, R⁹₂AlCl, R⁹AlCl₂, R⁹₃Al₂Cl₃, or R⁹AlO, wherein R⁹ is alkyl containing 1 to 25 carbon atoms.
 - 446. The process as recited in claim 445 wherein ${\ensuremath{\mathsf{R}}}^9$ contains 1 to 4 carbon atoms.
 - 447. The process as recited in claim 443 wherein said second compound is R⁹₃Al, R⁹₂AlCl, R⁹AlCl₂, or R⁹AlO, R⁹₃Al₂Cl₃, wherein R⁹ is alkyl containing 1 to 25 carbon atoms.
 - 448. The process as recited in claim 439 carried out at a temperature of about 25°C to about 100°C.
 - 449. The process as recited in claim 439 wherein a partial pressure of said ethylene is about atmospheric pressure to about 275 MPa.
 - 450. The process as recited in claim 439 wherein R^2 and R^5 are each independently hydrocarbyl, provided

that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

451. A process for the formation of linear α -olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

ethylene and a compound of the formula

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(III)

or

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20

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(VIXXX)

wherein:

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl;

 R^3 and R^4 are each independently hydrogen, substituted hydrocarbyl, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 T^1 is hydrogen or n-alkyl containing up to 38 carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the 484

conjugate acid of that compound (measured in water) is less than about 6;

U is n-alkyl containing up to 38 carbon atoms; and

X is a noncoordinating anion;

and wherein an $\alpha\text{-olefin}$ containing 4 to 40 carbon atoms is produced.

452. A process for the production of polyolefins, comprising, contacting, at a temperature of about 0° C to about $+200^{\circ}$ C, a compound of the formula

$$R^3$$
 N
 M
 A
 R^4
 R^5
 X

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XXXVII

and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

 ${\rm R}^2$ and ${\rm R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R¹⁷ is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at

least two saturated carbon atoms; R¹ is hydrogeh, or hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;

5 and provided that;

30

when norbornene or substituted norbornene is present, no other monomer is present; and when M is Pd a diene is not present.

- 453. The process as recited in claim 452 wherein 10 said temperature is about 20°C to about 100°C.
 - 454. The process as recited in claim 452 wherein said olefin is ethylene or a linear $\alpha\text{-olefin}$.
 - 455. The process as recited in claim 452 wherein said olefin is ethylene.
- 15 456. The process as recited in claim 452 wherein R² and R⁵ are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R³ and R⁴ are each independently hydrogen, hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring.
 - 457. The process as recited in claim 452 or 454 wherein a Lewis acid is also present.
- 458. The process as recited in claim 452 wherein M 25 is Ni(II).
 - 459. The process as recited in claim 452 wherein M is PD(II).
 - 460. The process as recited in claim 452 wherein said π -allyl or π -benzyl group is selected from the group consisting of

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

wherein R is hydrocarbyl.
461. A compound of the formula

 R^3 N N A R^4 R^5 X

XXXVII

wherein:

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M is Ni(II) or Pd(II);

A is a π -allyl or π -benzyl group;

 R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

each R^{17} is independently hydrocarbyl or substituted hydrocarbyl provided that any olefinic bond in said olefin is separated from any other olefinic bond or aromatic ring by a quaternary carbon atom or at least two saturated carbon atoms; R^1 is hydrogen, or

hydrocarbyl or substituted hydrocarbyl containing 1 to 10 carbon atoms;

and X is a weakly coordinating anion;
and provided that when M is Pd a diene is not
present.

462. The compound as recited in claim 461 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

463. The compound as recited in claim 461 wherein M is Ni(II).

464. The compound as recited in claim 461 wherein M is Pd(II).

465. The compound as recited in claim 461 wherein said π -allyl or π -benzyl group is selected from the group consisting of

 $\begin{array}{c} & & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$

wherein R is hydrocarbyl.

466. A compound of the formula

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wherein:

R³ and R⁴ are each independently hydrogen,

5 hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 R^{54} is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it:

each R⁵⁵ is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula $R^{17}CH=CHR^{17}$;

each R¹⁷ is independently hydrogen, saturated hydrocarbyl or substituted saturated hydrocarbyl; and X is a weakly coordinating anion;

and provided that when M is Ni, W is alkylene and each R¹⁷ is independently hydrogen or saturated hydrocarbyl.

 $467.\ \,$ The compound as recited in claim 466 wherein $\,$ 30 $\,$ R 3 and R 4 are each independently hydrogen or

hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring; and R^{54} is hydrocarbyl.

468. The compound as recited in claim 466 or 467 wherein each R^{55} is independently hydrogen or alkyl containing 1 to 10 carbon atoms.

469. The compound as recited in claim 466 wherein Z is neutral Lewis base.

470. The compound as recited in claim 469 wherein Z is a dialkyl ether.

10 471. The compound as recited in claim 466 wherein Z is R¹⁷CH=CHR¹⁷.

472. The compound as recited in claim 471 wherein each \mathbb{R}^{17} is independently hydrogen or alkyl.

473. The compound as recited in claim 471 wherein both of R^{17} are hydrogen.

474. The compound as recited in claim 466 wherein W is $-CH(CH_3)CH_2-$ or $-C(CH_3)_2CH_2-$.

475. The compound as recited in claim 471 wherein W is a divalent polymeric radical derived from the polymerization of $R^{17}CH=CHR^{17}$.

476. A process for the production of a compound of the formula

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25 comprising, heating a compound of the formula

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at a temperature of about -30°C to about +100° for a sufficient time to produce (XXXVIII), and wherein:

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

 ${
m R}^{54}$ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it;

each R⁵⁵ is independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

 R^{56} is alkyl containing 2 to 30 carbon atoms; T^{5} is alkyl;

W is alkylene containing 2 to 30 carbon atoms; Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the conjugate acid of that compound (measured in water) is

less than about 6; and

X is a weakly coordinating anion.

477. The process as recited in claim 476 wherein 25 R³ and R⁴ are each independently hydrogen or hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring; and R⁵⁴ is hydrocarbyl.

478. The process as recited in claim 476 or 472 wherein each R^{55} is independently hydrogen or alkyl containing 1 to 10 carbon atoms.

479. The process as recited in claim 476 wherein 2 is a dialkyl ether.

480. The process as recited in claim 476 wherein W is -CH(CH $_3$)CH $_2$ -.or -C(CH $_3$) $_2$ CH $_2$ -

481. The process as recited in claim 476, 477, 479 or 480 wherein T^5 is methyl.

482. A process for the polymerization of olefins, comprising, contacting a compound of the formula

10 (XXXVIII)

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and one or more monomers selected from the group consisting of ethylene, an olefin of the formula $R^{17}CH=CH_2$ or $R^{17}CH=CHR^{17}$, cyclobutene, cyclopentene, substituted norbornene, and norbornene,

wherein:

 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

20 R⁵⁴ is hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound directly to the imino nitrogen atom has at least two carbon atoms bound to it:

each R⁵⁵ is independently hydrogen,

25 hydrocarbyl, substituted hydrocarbyl, or a functional group;

W is alkylene or substituted alkylene containing 2 or more carbon atoms;

Z is a neutral Lewis base wherein the donating atom is nitrogen, sulfur, or oxygen, provided that if the donating atom is nitrogen then the pKa of the

conjugate acid of that compound (measured in water) is less than about 6, or an olefin of the formula R¹⁷CH=CHR¹⁷;

each R¹⁷ is independently hydrogen, saturated 5 hydrocarbyl or substituted saturated hydrocarbyl; and X is a weakly coordinating anion; and provided that:

when M is Ni, W is alkylene and each R^{17} is independently hydrogen or saturated hydrocarbyl;

and when norbornene or substituted norbornene is present, no other monomer is present.483. The process as recited in claim 482 wherein R³ and R⁴ are each independently hydrogen or hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene to form a ring; and R⁵⁴ is hydrocarbyl.

484. The process as recited in claim 482 or 483 wherein each R^{55} is independently hydrogen or alkyl containing 1 to 10 carbon atoms.

485. The process as recited in claim 482 wherein Z 20 is a dialkyl ether.

486. The process as recited in claim 482 wherein Z is $R^{17}CH=CHR^{17}$.

487. The process as recited in claim 482 wherein each R^{17} is independently saturated hydrocarbyl or hydrogen.

488. The process as recited in claim 482 wherein both of R^{17} are hydrogen.

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489. The process as recited in claim 482 wherein W is $-CH(CH_3)CH_2-$ or $-C(CH_3)_2CH_2-$.

490. The process as recited in claim 482 wherein said temperature is about 20°C to about 100°C.

491. The process as recited in claim 482 wherein said olefin is ethylene or a linear α -olefin.

492. The process as recited in claim 482 wherein said olefin is ethylene, propylene or a combination of ethylene and propylene.

493. The process as recited in claim 486 wherein said olefin is ethylene, propylene or a combination of ethylene and propylene.

- 494. The process as recited in claim 489 wherein 5 said olefin is cyclopentene.
 - 495. The process as recited in claim 482 wherein said olefin is cyclopentene.
 - 496. A homopolypropylene containing about 10 to about 700 $\Delta +$ methylene groups per 1000 methylene groups.
 - 497. The homopolypropylene as recited in claim 496 containing about 25 to about 300 $\delta +$ methylene groups per 1000 methylene groups.
 - 498. A homopolypropylene wherein a ratio of $\delta+:\gamma$ methylene groups is about 0.5 to about 7.
 - 499. The homopolypropylene as recited in claim 498 wherein said ratio is about 0.7 to 2.0.
- 500. A homopolypropylene in which about 30 to about 85 mole percent of monomer units are enchained in 20 an ω ,1 fashion.
 - 501. The homopolypropylene as recited in claim 500 wherein about 30 to about 60 mole percent of the monomer units are enchained in an ω ,1 fashion.
- 502. A process for the formation of linear α 25 olefins, comprising, contacting, at a temperature of about -100°C to about +200°C:

ethylene;

and a Ni[II] of

(VIII)

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 $\mbox{\ensuremath{R^2}}$ and $\mbox{\ensuremath{R^5}}$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom

bound to the imino nitrogen atom has at least two carbon atoms bound to it;

 $\rm R^3$ and $\rm R^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or $\rm R^3$ and $\rm R^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring and

wherein an $\alpha\text{-olefin}$ containing 4 to 40 carbon atoms is produced.

503. The process as recited in claim 502 wherein said linear α -olefin has the formula $H_2C=CHR^1$, wherein R^1 is n-alkyl containing 2 to 30 carbon atoms.

504. The process as recited in claim 502 wherein $\ensuremath{R^2}$ and $\ensuremath{R^5}$ are phenyl.

505. The process as recited in claim 502 wherein \mathbb{R}^3 and \mathbb{R}^4 are hydrogen, methyl or 1,8-naphthylylene.

506. The process as recited in claim 503 wherein \mathbb{R}^3 and \mathbb{R}^4 are hydrogen, methyl or 1,8-naphthylylene.

507. The process as recited in claim 502 carried out at a temperature of about 25°C to about 100°C.

508. The process as recited in claim 502 wherein a partial pressure of said ethylene is about atmospheric pressure to about 275 MPa.

509. The process as recited in claim 502 wherein R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.

30 510. A polymer blend comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and one other polymer.

511. A nonwoven fabric wherein at least some fibers comprise the polymer of claim 345, 349, 353,

35 354, 355, 358, 360 or 361.

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512. A shaped part comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

513. A sheet or film comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

514. A nonwoven fabric or microfiber comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

515. A laminate wherein one or more of the layers comprises the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

516. The laminate as recited in claim 511 wherein 10 a barrier layer is present.

517. A fiber comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

518. A foam or foamed object comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

519. A microporous membrane comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361.

520. The polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 which is crosslinked.

20 521. The polymer of claim 345, 349, 353, 354, or 355 which is heat treated.

522. The polymer as recited in claim 521 which has 20 percent or more crystallinity.

523. A composition comprising the polymer of claim 25 345, 349, 353, 354, 355, 358, 360 or 361 and a nucleating agent.

524. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and a flame ratardant.

30 525. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and an antioxidant.

526. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 and a filler

35 or reinforcer.

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527. A composition comprising the polymer of claim 345, 349, 353, 354, 355, 358, 360 or 361 which is electrically conductive.

528. A process, comprising, contacting, at a temperature of about -80°C to about $+20^{\circ}\text{C}$, a compound of the formula $(\eta^4\text{--}1,5\text{--COD})\text{PdMe}_2$ and a diimine of the formula

5

to produce a compound of the formula

10

$$R^3$$
 N
 Pd
 Me
 R^4
 R^5

(XXXXI)

wherein:

COD is 1,5-cyclooctadiene;

15

 ${
m R}^2$ and ${
m R}^5$ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

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 ${\rm R}^3$ and ${\rm R}^4$ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or ${\rm R}^3$ and ${\rm R}^4$ taken together are hydrocarbylene or substituted hydrocarbylene to form a ring.

529. The process as recited in claim 528 wherein said temperature is about -50°C to about +10°C.

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530. The process as recited in claim 528 wherein R^2 and R^5 are both 2-t-butylphenyl or 2,5-di-t-butylphenyl, and R^3 and R^4 taken together are 1,8-

naphthylylene, or \mathbb{R}^3 and \mathbb{R}^4 are both hydrogen or methyl.

- R^2 and R^5 are each independently hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^3 and R^4 are each independently hydrogen, hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene to form a ring.
- 10 532. The compound as recited in claim 232, 248, 253, 259, 267, 317, 334, 339, 461 or 466 wherein X is part of a heterogeneous support.
 - 533. The compound as recited in claim 532 wherein said heterogeneous support is montmorillonite.
- 15 534. The process as recited in claim 49, 97, 176, 199, 280, 299, 451, 452 or 482 wherein X is part of a heterogeneous support.
 - 535. The process as recited in claim 49, 97, 176, 199, 280, 299, 451, 452 or 482 wherein a polymerization catalyst is supported on a heterogeneous support.
- 20 catalyst is supported on a neterogeneous support.

 536. The compound as recited in claim 232, 248,
 253, 259, 267, 317, 334, 339, 461 or 466 which is
 supported on a heterogeneous support.
 - 537. The process as recited in claim 49, 97, 176, 199, 280, 299, 451, 452 or 482 wherein the
- 25 199, 280, 299, 451, 452 or 482 wherein the polymerization is run in the gas phase.

Č

- 538. The process as recited in claim 478 which is run in a fluidized bed reactor.
- 539. A flexible pouch made from a single or 30 multilayer film which comprises the polymer of claim 1, 3, 4, 6, 7, 332 or 343.
 - 540. The polymer of claim 1, 3, 4, 6, 332 or 343 grafted with a compound containing ethylenic unsaturation and a functional group.
- 541. The polymer as recited in claim 540 wherein said functional group is carboxyl, carboxylic anhydride, ester or a carboxylate salt.

542. A wrap packaging film having differential cling, comprising a film laminate having at least two layers;

an outer reverse layer which comprises a polymer of claim 1, 3, 4, 6, 7, 332 or 343, and a tackifier present in sufficent amount to impart cling properties; and

an outer obverse layer which has a density of at least about 0.916 g/mL and which has little or no cling; and

provided that a density of said outer reverse layer is at least 0.008 g/mL less than that of a density of said outer obverse layer.

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543. A fine denier fiber comprising the polymer of claim 1, 3, 4, 6, 7, 332 or 343.

544. A composition, comprising, a polymer of claim 1, 3, 4, 6, 7, 332 or 343 and an antifogging agent.

545. The process as recited in claim 13, 15 or 142 wherein said bidentate ligand or second compound is (XXX) and n is 2, all of R^{30} , R^{28} and R^{29} are hydrogen, and both of R^{44} and R^{45} are 9-anthracenyl.

546. The process as recited in claim 65 or 84 wherein said compound or said second compound is (XVII) and n is 2, all of R^{30} , R^{28} and R^{29} are hydrogen, and both of R^{44} and R^{45} are 9-anthracenyl.

547. The process as recited in claim 65 or 84 wherein said compound or said second compound is (XVII) and n is 2, all of R^{30} , R^{28} and R^{29} are hydrogen, both of R^{44} and R^{45} are 9-anthracenyl, M is Ni, and n is 2.

548. The compound or process as recited in claim 299 or 317 wherein M is Ni or Pd and m is 2.

549. The process as recited in claim 299 wherein M is Ni.

550. The process as recited in claim 49 wherein said olefin comprises cyclopentene.

551. The process as recited in claim 65 wherein said olefin comprises cyclopentene.

552. The process as recited in claim 452 wherein said olefin comprises cyclopentene.

553. The process as recited in claim 548 wherein said monomer comprises cyclopentene.

554. The process as recited in claim 17, 48, 124, 151, 156, 167, 180, 231, 298, 316, 550, 551, 552 or 553 wherein cyclopentene is a solvent.

555. The process as recited in claim 37 wherein:

R² and R⁵ are both 2,4,6-trimethylphenyl or

10 2,6-dimethylphenyl;

R³ and R⁴ taken together are 1,8-naphthylylene;

y and z are both 1;

M is Ni;

Q and S are both chloride, iodide or bromide;

15 and

5

m is 2.

556. The process as recited in claim 555 wherein said first compound is an alkylaluminum compound.

557. The process as recited in claim 556 wherein said alkylaluminum compound is ethylaluminum dichloride or methylaluminoxane.

558. The process as recited in claim 555, 556 or 557 wherein said monomer comprises cyclopentene.

559. The process as recited in claim 558 wherein 25 cyclopentene is a solvent.

560. The polymer as recited in claim 1, 3, 4, 6, 332 or 343 which has:

a melt flow ratio, I10/I2 ≥ 5.63;

a molecular weight distribution, Mw/Mn, defined

30 by the equation: $Mw/Mn \le (I10/I2)-4.63$; and

a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the

35 same I2 and Mw/Mn.

561. A composition comprising:

the polymer as recited in claim 1, 3, 4, 6, 332 or 343 which has:

a melt flow ratio, I10/I2, > or = 5.63; a molecular weight distribution, Mw/Mn, defined

by the equation: Mw/Mn < OR = (I10/I2)-4.63; and

a critical shear rate at onset of surface melt

fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I2 and Mw/Mn; and

at least one other: natural polymer; a synthetic

10 polymer chosen from the polymer of claims 1, 3, 4, 6,

332, or 343; or a conventional high density

polyethylene, low density polyethylene or linear low

density polyethylene polymer.

562. The polymer as recited in claim 1, 3, 4, 6, 332, 343, 383, 384, 385, 386 or 387 which has a melt flow ratio, I10/I2 ≥ 5.63, a molecular weight distribution, Mw/Mn, defined by the equation: Mw/Mn ≤ (I10/I2)-4.63, and a critical shear stress at onset of gross melt fracture of greater than about 400 kPa.

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